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OF
UNIRRADIATED SNAP FUELS
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THERMOPHYSICAL PROPERTIES
OF
UNIRRADIATED SNAP FUELS
(Title Unclassified)

By:

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ABSTRACT

Enthalpy and thermal diffusivity measurements were made on four SNAP fuels from room temperature to 900°C. The specific heats were determined from the enthalpy measurements, and thermal conductivities were calculated from the product of specific heat, thermal diffusivity, and density. Polynomial expressions were obtained for the evaluation of each of the properties as a function of temperature. The fuels investigated were zirconium - 10 wt % uranium alloys, hydrided to ratios of 1.58, 1.65, 1.70, and 1.81 H/Zr.

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I. INTRODUCTION

Reliable values of the thermophysical properties of the fuel are required to predict the operating temperatures and temperature response of SNAP reactors. Among the most important of these properties are the thermal conductivity, specific heat, and thermal diffusivity. This report describes the most recent measurements of these quantities for fuel of four hydrogen contents: 1.58, 1.65, 1.70, and 1.81 H/Zr.*

A considerable number of investigations⁽¹⁻⁴⁾ have been made of these properties for the Zr-H and Zr-H-U systems.† Little of the work on zirconium hydrides is applicable to SNAP fuel. The addition of small amounts of uranium has been shown⁽³⁾ to drastically alter the thermal conductivity of zirconium and its hydrides. Although it is possible, by Knoop's rule, to estimate the effect on the specific heat of zirconium hydrides due to the addition of uranium, such calculations are only estimates. In fact, similar calculations⁽⁵⁾ on zirconium hydrides yield estimated values which are lower than experimental values by ~10% at 350°C, and diverge still more with increasing temperature.

Conventional studies of thermophysical properties are usually conducted in vacuum or an inert gas atmosphere. These techniques are not applicable to metal hydrides, due to the high mobility of hydrogen in these materials and to the reversible dissociation of the hydrogen. For example, in the direct measurement of thermal conductivity, it is necessary to establish a heat flux by imposing a thermal gradient on the sample; the conductivity is then measured at an "average" temperature. In hydrides, however, this direct method cannot yield meaningful results, since the hydrogen will redistribute under the influence of the thermal gradient, thus forming a concentration gradient; so that one has a spectrum of compositions, rather than a homogenous alloy. Although the "average" composition of the material may be identical to the initial uniform concentration, the directly measured value of conductivity will be dependent on the thickness of the specimen, due to the highly sensitive dependence of transport properties on hydrogen content. This dependence is strikingly illustrated

*H/Zr, in this report, indicates an "effective" hydrogen-to-zirconium ratio, calculated on the basis that the zirconium added to the fuel as ZrC does not hydride.

†References 1 and 2 are comprehensive bibliographies on the properties of these systems to early 1964.

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by the work of Bickel,⁽⁶⁾ who found that the electrical conduction of zirconium hydrides ranges from primarily hole conduction to primarily electronic conduction, depending upon the hydrogen content. Fortunately, the direct measurement of thermal conductivity is unnecessary, since it can be expressed as the product of the specific heat, thermal diffusivity, and density, all of which can be directly measured with considerable accuracy.

In prior studies of SNAP fuel,^(3-5, 7) the specific heat has been determined by a pulse heating technique. Although, in one study,⁽⁴⁾ this technique was shown to give results comparable to those obtained by calorimetric methods, it is open to criticism. The values obtained by this method are very sensitive to the electrical resistance of the specimen, which, in turn, can be altered by microscopic flaws in the fuel which may be introduced between the measurement of resistance and the determination of specific heat. It is also questionable whether equilibrium conditions are maintained during the extremely rapid heating of the specimen. Furthermore, the method often results in the destruction of the specimen, so that reproducibility of results depends upon the availability of several specimens which are essentially identical, both macroscopically and microscopically. Finally, the precision of the pulse heating method is less than that of calorimetric methods, because the maximum specimen size is considerably less than that which can be used in calorimetry. In the present work, specific heat was determined by calorimetry to avoid these objections, and because the method is essentially independent of both the macroscopic and microscopic structure of the specimen. It should be noted that all of the experimental work reported here was performed with careful attention to accurate measurement of all factors which are known to affect the thermophysical properties of hydrides and, in particular, to the composition of the fuel as functions of temperature and pressure.

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II. MATERIALS

A. NONHYDRIDED ALLOY

The SNAP fuel alloy used in this work was representative of that used in SNAP reactors, except that normal uranium was substituted for the enriched uranium required for reactors. The alloy was produced, but not used, for an earlier program⁽⁴⁾ by a triple-arc-melt and double-extrusion process, with a final extrusion diameter of 1.22 in. Four rods, 12.5 in. long, from Extrusion Number 398 were used. Chemical analyses of the rods yielded the results given in Table 1.

TABLE 1
CHEMICAL ANALYSIS OF NONHYDRIDED ALLOY

Element	Concentration (ppm)	Element	Concentration (ppm)	Element	Concentration (ppm)
Al	<50	Cu	<20	Si	<50
B	<0.5	Fe	375	Sn	<2
Ba	<5	Hf	<200	Ti	<50
Be	<1	Mg	<5	V	<10
Bi	<2	Mn	<15	Zn	<25
Ca	<20	Mo	<5	W	14
Cd	<0.5	Na	<5	H	9
Co	<2	Ni	<10	O	905
Cr	100	Pb	<5	N	70
Normal Uranium - 10.30 wt %			Carbon - 0.15 wt %		

Approximately 10 in. of each rod was centerless ground to 0.800 ± 0.003 in. in diameter before hydriding. The portion of the rod with reduced diameter was then cut into three pieces, to be used for the preparation of experimental specimens; the remaining portion was reserved for additional chemical analysis after hydriding and for archive purposes.

B. HYDRIDING

Each of the four rods was hydrided separately, using ultrapure hydrogen (10 ppm total impurities). The four pieces of a given rod were placed in a retort and hydrided simultaneously, using standard production procedures.⁽⁸⁾ The hydrogen content of each piece was determined by the weight gain, each having been weighed to ± 1 mg before and after hydriding. The density of each piece was measured by the liquid displacement method. Table 2 gives the hydrogen content and density of the archive specimens and of those pieces from which diffusivity and specific heat data were obtained; no diffusivity specimens were prepared for 1.81 H/Zr fuel, because previous data⁽⁴⁾ were considered sufficiently accurate. A portion of each archive specimen was analyzed destructively for hydrogen, uranium, carbon, and oxygen. The hydrogen analyses gave results which agreed within ± 0.02 H/Zr with the values given in Table 2. The uranium, carbon, and oxygen analyses agreed almost exactly with the values given in Table 1, after adjustment for the added hydrogen. Since all pieces from

TABLE 2
INITIAL HYDROGEN CONTENT AND DENSITY

Rod Number	Purpose	Hydrogen Content		Density (gm/cm ³)
		(wt %)	(H/Zr)	
4	Archive	1.536	1.597	6.112
	Specific Heat	1.538	1.599	6.111
	Diffusivity	1.542	1.603	6.111
3	Archive	1.561	1.623	6.104
	Specific Heat	1.569	1.632	6.105
	Diffusivity	1.566	1.628	6.103
2	Archive	1.679	1.748	6.076
	Specific Heat	1.687	1.756	6.074
	Diffusivity	1.695	1.765	6.075
5	Archive	1.724	1.796	6.077
	Specific Heat	1.740	1.813	6.075

a given rod were hydrided together, it is reasonable to assume that analyses of the remaining pieces would also yield results in agreement with Tables 1 and 2.

C. SPECIMEN PREPARATION

1. Specific Heat Specimens

Two of the three pieces from each rod were centerless ground to 2.00 cm (0.787 ± 0.002 in.) in diameter. A thin slice was then carefully removed from each end for metallographic examination. In every case, this examination showed a uniform radial structure, as evidenced by the appearance and distribution of the grains of the two phases which are present in the fuel at these hydrogen concentrations. The specimens from Rods 3 and 4 appeared to be entirely δ phase, with essentially uniform equiaxed grains; the specimens from Rod 2 showed a uniform distribution of δ and ϵ grains; and the specimens from Rod 5 were entirely ϵ phase, with essentially uniform grain sizes. Thus, it is concluded that no significant radial concentration gradient occurred as a result of hydriding, and that the grinding operation produced no appreciable loss of hydrogen from the surface. It should be noted that care was taken during all grinding operations of these and of the diffusivity specimens to avoid heating of the material and the consequent loss of hydrogen.

The final specimens (~ 7 cm long) were obtained by centerless grinding of both ends to a truncated cone with an apex angle of 60° ; the diameter at the ends was thus reduced to ~ 1 cm. The conical ends were required to facilitate raising and lowering the specimens in the calorimeter (see Section III).

2. Thermal Diffusivity Specimens

About 1 in. of the third piece from each rod was centerless ground to 0.250 ± 0.005 in. in diameter for the preparation of diffusivity specimens. A thin slice was removed from each piece and metallographically examined, with the same results reported previously. A minimum of six wafers was fabricated from each of the 0.25 in. pieces, ranging from 0.070 to 0.105 in. thick. The faces of the wafers were carefully ground to be parallel to 0.001 in. or better. Again, great care was taken to avoid heating the wafers. Each of the wafers was examined under 10X magnification and by gamma-graph techniques to detect small surface cracks and subsurface voids. All wafers were found to be free of cracks and macroscopic voids.

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III. SPECIFIC HEAT

Drop calorimetry is probably the simplest and most generally applicable method of determining high-temperature specific heats. In principle, the method consists of determining the enthalpy change in a material by measuring the heat (H) absorbed by a cool receiver after it receives a heated sample of unit mass. The specific heat (c_p) of the sample is then obtained from the temperature derivative of the enthalpy change, i.e.,

$$c_p = dH/dT \quad \dots (1)$$

This method has several advantages over pulse heating and other methods:

- 1) The size and shape of the specimen are limited only by the physical dimensions of the calorimeter.
- 2) The results do not depend on the previous measurement of any property of the sample other than its mass.
- 3) The specimen need not be physically sound (i.e., voids and cracks are of no consequence, since they do not contribute to the mass of the specimen).
- 4) The same specimen can be used repeatedly for measurements at any temperature within the solid range of the material.
- 5) The precision of the measurements can be made as great as necessary by the use of sensitive temperature sensors (e.g., many element thermopiles), large samples, and a large receiver.
- 6) Specimen heating times can be made sufficiently long to ensure as close an approach to equilibrium as desired.

The most serious limitation of the method is that cooling of the sample may be too rapid to permit phase changes, so that the sample is quenched in a non-equilibrium state and evolves less heat than equilibrium conditions would yield. The calorimeter used in this work was designed to eliminate this problem. Its receiver can be heated to elevated temperatures, thus eliminating the necessity of passage of the sample through phase boundaries. Because this instrument is unique, it will be described in some detail.

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A. CALORIMETER

The drop calorimeter used in this work was specifically designed for the measurement of the specific heats of metal hydrides. It can be operated with sample temperatures as high as 1650°C and at pressures from 10^{-8} to 10 atm. The temperature of the receiver can be varied from room temperature to 650°C. Figure 1 is a simplified cross section of the calorimeter, the four principal parts of which are the furnace, the transition zone, the receiver, and the dropping mechanism.

Figure 1. Drop Calorimeter

1. Furnace

The furnace was molybdenum wound, with bubbled alumina insulation. Heat losses were further reduced by molybdenum heat shields adjacent to the furnace winding. The central portion of the furnace was lined with a thick-walled Armco-iron tube to provide a minimum vertical temperature gradient in the sample region.

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2. Transition Zone

The transition zone was heated to reduce heat losses from the receiver along the supporting connection between the two. Movable heat shields (trap doors) near the top and bottom of the transition zone minimized convection losses from the receiver and prevented furnace radiation from entering the receiver. These shields were operated by a rotary solenoid, and could be opened and closed in a few seconds to allow the specimen to pass through the transition zone into the receiver.

3. Receiver

The receiver was a thick-walled copper cylinder, weighing about 100 lb. It was vacuum insulated from a surrounding heavy copper shell (the receiver guard) which was maintained at the receiver temperature to provide additional thermal shielding of the receiver. The temperatures of the transition zone and receiver guard were differentially controlled with respect to the receiver temperature, so that they followed it and maintained receiver heat losses at negligibly low values. Proper adjustment of the transition zone and receiver guard temperatures yielded receiver time constants of several hours.

A heating coil in the bottom of the receiver served a dual purpose. It was used for electrical calibration of the heat capacity of the receiver. It could also be used to adjust the receiver temperature to any value from room temperature to 650°C, in order to prevent phase transformations within the specimens upon cooling.

4. Drop Mechanism

The drop mechanism permitted repeated measurements of a given specimen, without the necessity of opening the calorimeter between measurements. The specimen was suspended on a molybdenum cable (6 strands of 10-mil wire) which was attached to a magnetic armature inside a long, nonmagnetic thimble (copper) located above the furnace. The armature was supported by permanent magnets external to the thimble and fitted with suitable pole pieces to concentrate the magnetic field at the armature. The magnet assembly was driven up or down by a linear motor, thus raising or lowering the specimen.

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5. Temperature Control

Temperature sensing in the furnace was provided by three Geminol* thermocouples which were spot welded to the furnace side of the Armco-iron tube on 2-in. centers. The center thermocouple was used for measurement and control of the furnace temperature, using a null-balance controller with a controlled rectifier output. The temperature was thus maintained within $\pm 0.5^{\circ}\text{C}$ with pressures ≤ 1 atm, and within $\pm 3^{\circ}\text{C}$ at pressures of ~ 10 atm. The outer thermocouples were used to measure the longitudinal temperature profile of the furnace; this profile was controlled by manual adjustment of a secondary heater to correct for end losses. Tests were performed, using stainless steel, the thermal conductivity of which is nearly the same as that of the fuel; three thermocouples were welded to this specimen on 1-in. centers. The results of these tests indicated that the maximum temperature variation over the length of hydrided specimens would not exceed 5°C . Since it was not practical to attach thermocouples to the fuel specimens, their temperatures were inferred from the furnace temperature, with an estimated error of 10°C .

The temperature sensors in all regions of the calorimeter other than the furnace were Chromel-Alumel elements, fabricated from calibrated wire. The control thermocouples for the transition zone and receiver guard heaters were connected differentially to thermocouples imbedded in the receiver wall. The controllers were of the null-balance type, with band width control to minimize temperature overshoot.

The heavy wall of the receiver and the proper adjustment of the transition zone heater provided essentially zero longitudinal and circumferential temperature gradients over the length of the receiver. The absence of such gradients was verified by several thermocouples, imbedded in the receiver wall at various locations. The temperature rise of the receiver upon receiving a specimen was measured by means of a 10-element thermopile, in conjunction with a precision potentiometer; this system provided a sensitivity of 0.0025°C . However, since the thermopile was not calibrated, the error in the absolute temperature of the receiver was estimated at 1°C .

*Nickel-base alloys which are stable in hydrogen (Driver-Harris Co.)

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6. Pressure Control

The calorimeter was designed for both vacuum and pressure operation. All seals and external walls were water cooled to maintain them at near room temperature. One of the two vacuum systems was used only to maintain the vacuum insulation between the receiver and the receiver guard. The primary 6-in. vacuum system permitted rapid evacuation, to $\leq 10^{-5}$ torr, of the furnace, transition zone, and receiver. Both vacuum systems were connected to a single exhaust line which was vented to the outside of the building to prevent accumulation of hydrogen in the laboratory; during operation, this line was continuously purged with argon to prevent any mixing of hydrogen and air in the building. Gases in the calorimeter, at pressures up to 1 atm, were exhausted through the 6-in. vacuum system. For pressures above 1 atm, the gases were first exhausted into the vent through a 3/8-in. copper line fitted with a solenoid valve for rapid release and a check valve to prevent back-streaming.

Gas pressures within the calorimeter were controlled manually. They were measured below 450 torr by two calibrated precision dial manometers; a 0 to 100 torr manometer, graduated in units of 0.5 torr, and a 0 to 450 torr manometer, graduated in units of 1 torr. Pressures above 450 torr were measured by a 0 to 150 psia pressure transducer; this transducer was linear to 0.3% of full scale, and was sensitive to 0.03 psia (1.55 torr).

B. CALIBRATION

Before the calorimeter could be used to determine the specific heat of SNAP fuel, it was necessary to determine the response of the receiver to additions of heat at the temperature ranges over which it would be operated. The reference phase diagram⁽⁹⁾ at the start of this work is given in Figure 2, and is based on the results of several investigations. Since the phase boundaries for hydrogen contents ≥ 1.58 H/Zr were expected to be essentially vertical, it was considered unnecessary to use elevated receiver temperatures. Therefore, the receiver response was determined only for the range of 34 to 50°C. Two independent methods were used for this calibration: (1) by supplying a known amount of energy to the receiver through its heating coil, and (2) by normal operation, using a copper specimen.

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Figure 2. Zirconium-Hydrogen Phase Diagram

The electrical method is based on the expression

$$\dot{h} = \int E I dt = \int E(e) I(e) \frac{dt}{de} de, \quad \dots (2)$$

where:

h = heat added to the receiver

E = voltage drop across the heater

I = current in the heater

e = thermopile emf

t = time

The receiver characteristic which is required for calibration is given by the derivative of this expression, viz.

$$\frac{dh}{de} = E(e) I(e) \frac{dt}{de}. \quad \dots (3)$$

To determine dh/de , power was supplied continuously to the receiver and E , I , and e were measured at regular intervals of t . The voltage drop was maintained at 10 ± 0.001 v, using a voltage-regulated, solid-state power supply; it

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was measured with a precision potentiometer. The heater current, ~ 4.5 amp, was measured to 1 part in 10^4 by measuring the potential drop across a 0.01% shunt with a precision potentiometer. The thermopile emf was measured to $1 \mu\text{v}$ ($\sim 0.0025^\circ\text{C}$). The values of dh/de were found to be essentially constant at $1.0010 \pm 0.0025 \text{ cal/mv}$.

The second method, that of dropping a known specimen, yields the expression

$$m \int_{(T_0 + \delta)}^T c_p(\theta) d\theta = h = \int_{e_0}^{e_1} \frac{dh}{de} de, \quad \dots (4)$$

where:

m = mass of the specimen

c_p = specific heat of the specimen

θ = temperature of the specimen

T = temperature of the furnace

T_0 = initial temperature of the receiver

δ = increase in the receiver temperature after a drop

e_0 = initial thermopile emf

e_1 = final thermopile emf

Since δ was found to be only 0.1% of $T - T_0$, and since dh/de had been found to be essentially constant in the electrical calibration, the receiver characteristic can be obtained from this expression as

$$\frac{dh}{de} = \frac{m}{e_1 - e_0} \int_{T_0}^T c_p(\theta) d\theta. \quad \dots (5)$$

Five calibration drops were made to room temperature from temperatures between 200 and 600°C , using 135.6 gm of copper. The initial receiver temperature was slightly higher for successive drops, but remained within the 34 to 50°C range. The copper was not well characterized, so that its specific heat

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may have been in error by at least 1% from the values⁽¹⁰⁾ used in the integration of Equation 5. The value obtained for dh/de , 1.016 cal/mv, is therefore in agreement with the value found in the electrical calibration. Since the precision of the electrical calibration was considerably greater, the value of 1.0010 cal/mv was used in the determination of the specific heats of fuel.

C. EXPERIMENTAL TECHNIQUE

The desired hydrogen content for each specimen ($H/Zr = 1.58, 1.65, 1.70$, or 1.81) was obtained in the calorimeter. After suspending the specimen in the furnace, the calorimeter was evacuated to $\leq 10^{-5}$ torr and purged a minimum of three times with ultrapure hydrogen. The specimen was then heated to 600 to 650°C for a minimum of 30 min* and the hydrogen overpressure maintained at the level corresponding to the desired composition. The required pressures were obtained from a tabulation at 10° intervals, based on Johnson's⁽¹¹⁾ isochores, and are given in Figure 3.

After the hydrogen content was adjusted, the specimen was dropped (under gravity with electromagnetic braking) into the room-temperature receiver. Each specimen was subjected to a series of such drops, from furnace temperatures ranging from 200 to 900°C, except that the maximum temperature of 1.81 H/Zr fuel was limited to 760°C by the 10-atm limitation of the calorimeter. Before each drop, the hydrogen overpressure was adjusted to the level required for the new temperature, and was maintained at that level until the furnace temperature had remained constant for 20 to 30 min. During each drop, the heat shields in the transition zone were opened for only 3 to 4 sec to permit passage of the specimen. The thermopile emf was measured immediately before the drop, at intervals of 1 min for 10 min after the drop, and then at 5-min intervals until thermal equilibrium was established between the specimen and the receiver (20 to 40 min). Equilibrium was assumed to have been reached when the temperature decay curve essentially matched the curve obtained during calibration of the receiver.

*Using equations for diffusion in cylinders, it can be shown that this time was sufficient to adjust all specimens used to the desired hydrogen content within ± 0.0006 H/Zr.

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Figure 3. Dissociation Pressure of SNAP Fuels

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A detailed thermal analysis⁽¹²⁾ was performed before the start of the experimental work. This analysis showed that, in most cases, cooling of the specimen would be sufficiently rapid to maintain the hydrogen content within $\pm 0.005 \text{ H/Zr}$ without a reduction in the hydrogen overpressure. However, it also showed that, for several of the drops from the higher furnace temperatures, it would be necessary to reduce the pressure to $\sim 1 \text{ atm}$ within $\sim 20 \text{ sec}$ after the drop. This was accomplished by means of the bypass system described earlier.

D. DETERMINATION OF ENTHALPY CHANGE AND SPECIFIC HEAT

To determine the specific heat of each specimen, the data from each drop was analyzed to obtain the enthalpy change for the drop. The enthalpy changes for each composition were then subjected to a least squares treatment, using a digital computer, to obtain enthalpy as a polynomial function of temperature. The specific heat was then obtained from the derivative of the expression for enthalpy.

The enthalpy change during each drop is given by the expression

$$H(T, \theta_2) = \frac{1}{m} \int_{e_1}^{e_2} \frac{dh}{de} de = \frac{1}{m} \frac{dh}{de} (e_2 - e_1) , \quad \dots (6)$$

where

$H(T, \theta_2)$ = enthalpy change per unit mass from T to θ_2

T = furnace temperature

θ_2 = the receiver temperature after cooling of the specimen

h = receiver enthalpy change

e_1 = thermopile emf before the drop

e_2 = thermopile emf after cooling of the specimen

m = mass of the specimen

Since the initial receiver temperature varied in each series of drops, a correction was made to normalize all drops to the same initial receiver temperature, θ_0 . An additional correction was required to account for the

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contribution of the molybdenum suspension system. The mass of the wire (m_w) was small, compared to that of the specimen (~ 0.5 gm vs ~ 115 gm), so that its average specific heat ($\bar{c}_w$) was used to determine its heat contribution over the temperature range T to θ_2 . After applying these corrections, the expression for the enthalpy change during a drop becomes

$$H(T, \theta_0) = \frac{1}{m} \frac{dh}{de} (e_2 - e_1) - m_w \bar{c}_w (T - \theta_2) + \left. \frac{dH}{d\theta} \right|_{\theta_0} \frac{d\theta}{de} (e_2 - e_0) \quad , \quad \dots (7)$$

where $\left. \frac{dH}{d\theta} \right|_{\theta_0}$ is the specific heat of the sample at θ_0 , and e_0 is the thermopile

emf at the same temperature. All data were normalized to $\theta_0 = 34^\circ\text{C}$, because this was approximately the initial receiver temperature in each series of drops. The use of 34° , rather than 0°C , as the reference temperature does not affect the value of specific heat, since the latter is the derivative of enthalpy with respect to temperature. The specific heat at 34°C was obtained from earlier work on 1.81 H/Zr fuel.⁽⁴⁾ Although the specific heat at 34° does vary with composition, the use of the value 0.072 cal/gm- $^\circ\text{C}$ for all compositions leads to a negligible error. The maximum error occurs in the case of 1.58 H/Zr fuel, for which the specific heat is ~ 0.09 cal/gm- $^\circ\text{C}$. In this case, the use of the lower value results in an error of only 0.3% in the enthalpy change at 200°C and $<0.01\%$ at 900°C .

E. RESULTS AND DISCUSSION

The enthalpy data (see Appendix I) were subjected to a polynomial least squares treatment which yielded third order polynomials as the best fit, the criterion for best fit was a minimum standard deviation. These polynomials are given in Figures 4a, b, c, and d for H/Zr = 1.58, 1.65, 1.70, and 1.81, respectively. The coefficients and standard deviations of the polynomials are given in Table 3. These standard deviations yield a probable error (at 95% confidence limits*) at reactor operating temperatures (500 to 900°C) of $\sim 2\%$ for the three lower compositions and $\sim 3\%$ for 1.81 H/Zr.

*See Appendix II for definition and method of calculation.

a. 1.58 H/Zr Fuel

c. 1.70 H/Zr Fuel

b. 1.65 H/Zr Fuel

d. 1.81 H/Zr Fuel

Figure 4. Enthalpy Change

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TABLE 3
ENTHALPY OF SNAP FUELS
(H = 0 at 34°C)

$$H(\text{cal/gm}) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 \quad (t = ^\circ\text{C})$$

H/Zr	a_0	$a_1 \times 10^2$	$a_2 \times 10^5$	$a_3 \times 10^8$	Standard Deviation
1.58	-3.30 ± 0.50	9.04 ± 0.53	1.7 ± 1.4	4.3 ± 1.0	0.70
1.65	-2.22 ± 0.47	7.13 ± 0.46	7.3 ± 1.2	0.18 ± 0.93	0.68
1.70	-2.39 ± 0.49	6.86 ± 0.59	8.6 ± 1.6	-0.80 ± 1.1	0.65
1.81	-2.62 ± 0.87	7.4 ± 1.0	8.4 ± 3.1	-1.2 ± 2.6	1.10

The only previous measurement of enthalpy changes in SNAP fuel was that of Vetrano et al.⁽⁴⁾ for 1.81 H/Zr, the results of which are indicated in Figure 4d (the reference temperature for their work was 0°C). For the range of 0 to 500°C, the differences between the two curves are equal to the coefficient (a_0) given for 1.81 H/Zr in Table 3. Thus, for this temperature range, the results of the two studies are essentially identical. The deviation of the curves above this range is attributed to the difference in the number of measurements; in the present work, 12 of the 21 data points were obtained in the range of 500 to 760°C; whereas, in the earlier work, only three points were obtained above 500°C (599, 651, and 654°C). Thus, since the precision of the individual measurements was comparable in the two studies, the results obtained here are probably more nearly correct.

Although the coefficients of the four polynomials indicate that the enthalpy changes are nearly the same for the four compositions, it was considered more appropriate to treat each composition separately. This decision was based on the fact that specific heat would be expected to depend on the number of atoms, and should therefore be a function of hydrogen content.

The specific heat for each composition is obtained from the derivative, with respect to temperature, of the expression for the enthalpy change. The resulting second order polynomials are shown in Figures 5a, b, c, and d; and their coefficients are given in Table 4. The standard deviations given in this table were obtained by the method described in Appendix II, and are expected

TABLE 4
SPECIFIC HEAT OF SNAP FUELS
 $c_p(\text{cal/gm-}^\circ\text{C}) = a_0 + a_1t + a_2t^2$

H/Zr	$a_0 \times 10^2$	$a_1 \times 10^4$	$a_2 \times 10^8$	Standard Deviation
1.58	9.04 ± 0.53	0.34 ± 0.20	13.0 ± 1.7	0.003
1.65	7.13 ± 0.46	1.47 ± 0.17	0.5 ± 1.6	0.003
1.70	6.86 ± 0.59	1.71 ± 0.23	-2.4 ± 1.9	0.003
1.81	7.4 ± 1.0	1.67 ± 0.44	-3.5 ± 4.5	0.004

to be valid at reactor operating temperatures. The corresponding probable errors at 95% confidence limits are $\sim 4\%$ for the three lower compositions and $\sim 6\%$ for 1.81 H/Zr fuel.

Earlier results,⁽³⁾ obtained from pulse heating of 1.58 H/Zr fuel, are indicated in Figure 5a. The discontinuities in those results coincide with discontinuities in the resistivities of the specimens used. The origin of the discontinuities is not known. They cannot be due to phase transformations, since it has been shown⁽¹³⁾ that fuel of this composition remains in the single-phase δ region, over the temperature range of the discontinuities. The results obtained in the present work are considered to be more accurate, because the precision of the calorimetric method is greater than that of the pulse heating method, and is not affected even by macroscopic flaws.

The results obtained by Vetrano et al.⁽⁴⁾ for 1.81 H/Zr are given in Figure 5d. Their values are a weighted average of calorimetric and pulse heating data, with greater weight assigned to the calorimetric data. Within the range of their results, the maximum difference between the two curves is $\sim 7\%$, well within the estimated accuracies of the two studies. The discrepancy is again attributed to the four-fold difference in the amount of high-temperature data obtained in the studies.

A recent detailed investigation, at elevated temperatures, of the phase boundaries in the high-hydrogen region of SNAP fuel⁽¹³⁾ indicates that 1.65 H/Zr and 1.70 H/Zr fuel undergo a transformation from the two-phase ($\delta + \epsilon$) region to the single-phase δ region at 150 to 200°C and 425 to 480°C, respectively, and that 1.81 H/Zr fuel transforms from ϵ to δ at $\sim 685^\circ\text{C}$. Since

a. 1.58 H/Zr Fuel

c. 1.70 H/Zr Fuel

b. 1.65 H/Zr Fuel

d. 1.81 H/Zr Fuel

Figure 5. Specific Heat

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discontinuities in slope or magnitude were not apparent in the enthalpy data, it was believed that the heats of transformation were small. However, even small heats of transformation should affect the specific heat. Accordingly, the enthalpy data for all compositions were fitted to fourth order polynomials, in an attempt to detect subtle effects due to the phase transformations. It was observed that the uncertainties in the coefficients of t^2 were approximately twice the values of the coefficients in the cases of 1.65 and 1.70 H/Zr fuel, and nearly equal to the coefficient in the case of 1.81 H/Zr fuel. Derivatives of these expressions yielded S-shaped curves for the specific heats of 1.65 and 1.70 H/Zr fuel, with inflections at ~ 200 and $\sim 450^\circ\text{C}$, respectively. The absence of an inflection in the case of 1.81 H/Zr fuel may be due to the fact that only three data points were obtained near or above the transformation temperature, so that the weighting of the high-temperature data was not sufficient to permit resolution of a rapid change by least square methods. These observations suggest that the transformations observed in the phase study may have appreciable effects on the specific heats, particularly for 1.65 and 1.70 H/Zr fuel. Whether this is indeed true can best be determined by repeating the investigations, using elevated receiver temperatures. (It should be noted that such a technique is not possible with 1.81 H/Zr fuel, since the maximum receiver temperature is below the transformation temperature.) Unfortunately, such a study is beyond the scope of the present work.

The specific heats given by the quadratic expressions (Table 4) were fitted to a theoretical model,⁽¹⁴⁾ in which the fuel was treated as a diatomic lattice, with the zirconium and hydrogen atoms considered to be Debye and Einstein oscillators, respectively. The agreement between the polynomial and theoretical model was very good, for all compositions except 1.58 H/Zr. The method and the results of the theoretical treatment are given in Appendix III.

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IV. THERMAL DIFFUSIVITY

The pulsed laser method⁽¹⁵⁾ was used for thermal diffusivity measurements on 1.58, 1.65, and 1.70 H/Zr fuel. In this method, thermal diffusivity is determined from the temperature history of the rear face of a wafer, following impingement of a pulse of energy on the front face. For valid results the following conditions must hold:

- 1) The energy impulse must be uniformly distributed over the face of the wafer.
- 2) The duration of the pulse must be negligibly small, compared to the characteristic temperature rise time of the specimen.
- 3) The energy transfer must be axially directed through the specimen.
- 4) The specimen temperature must be independent of heat losses for a period that is long, compared to the time required for the pulse to pass through the wafer. When these conditions are satisfied, the thermal diffusivity (α) can be obtained from the expression

$$\alpha = 0.139 \ell^2 / t_{1/2} \quad , \quad \dots (8)$$

where ℓ is the thickness of the wafer, and $t_{1/2}$ is the half-time (i.e., the time required for the temperature of the rear face to reach one-half of its maximum value, following the energy pulse). Techniques have been developed^(16,17) for applying necessary corrections in those cases where heat losses from the specimen are significant, or where the duration of the energy pulse is too long.

A. APPARATUS AND METHOD

Details of the apparatus and method used in determining the thermal diffusivity of metal hydrides have been reported,^(3,4) so only a brief description will be given here.

The specimens were in the form of small discs, 0.250 in. in diameter, with thicknesses as given in Table 5. The specimens were mounted in a stainless steel holder, by means of three pins symmetrically located around the

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TABLE 5
THERMAL DIFFUSIVITY SPECIMEN DATA

H/Zr	Specimen Number	Thickness (cm)
1.58	398-4-2-3	0.1920
	398-4-2-1	0.1895
1.65	398-3-4-6	0.1869
	398-3-4-4	0.1874
	398-3-4-1	0.2581
1.70	398-2-4-6	0.1816
	398-2-4-3	0.1849
	398-2-4-2	0.1984

circumference. Geminol thermocouple wires (3-mil) were spot welded to the center of the back face, about 1/16 in. apart. The specimen and holder were then placed within a stainless steel tube furnace, which was designed for operation up to 1000°C with internal hydrogen pressures in excess of 6000 torr. The system could be evacuated to $<2 \times 10^{-6}$ torr and backfilled with ultrapure hydrogen. Gas pressures were measured with two calibrated precision dial manometers: a 0 to 50 torr manometer, graduated in units of 0.2 torr, and a 0 to 6000 torr manometer, graduated in units of 10 torr.

The desired hydrogen content for each specimen was obtained in the apparatus. The wafer was first heated to temperatures $>600^{\circ}\text{C}$ and maintained at temperature for several minutes with a hydrogen overpressure corresponding to the desired composition⁽¹²⁾ (see Figure 3). Diffusivity measurements were then made at selected temperature intervals, generally during the cooling cycle. When the specimen temperature and hydrogen pressure were stabilized at appropriate values, the front face of the wafer was subjected to a short (1.5 msec) pulse from the laser. The output of the thermocouple was displayed on an oscilloscope and photographically recorded.

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TABLE 6
THERMAL DIFFUSIVITY OF SNAP FUELS
 $\alpha(\text{cm}^2/\text{sec}) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 \quad (t = ^\circ\text{C})$

H/Zr	$a_0 \times 10^2$	$-a_1 \times 10^4$	$a_2 \times 10^7$	$-a_3 \times 10^{10}$	Standard Deviation
1.58	8.81 ± 0.08	1.54 ± 0.07	1.99 ± 0.18	1.00 ± 0.13	0.0012
1.65	9.11 ± 0.06	1.36 ± 0.06	1.74 ± 0.16	0.94 ± 0.12	0.0017
1.70	8.93 ± 0.06	1.26 ± 0.06	1.60 ± 0.16	0.88 ± 0.12	0.0015
1.81*	11.12 ± 0.05	2.08 ± 0.06	3.47 ± 0.21	2.37 ± 0.19	

*From "best" values given in Reference 4

B. RESULTS AND DISCUSSION

The data obtained for the three fuel compositions studied in this work are given in Appendix I. For each composition, the data were subjected to a polynomial least squares treatment, using a digital computer. In each case, a third order polynomial was found to give the best fit, based on the standard deviations. The curves corresponding to these polynomials are given in Figures 6a, b, and c for 1.58, 1.65, and 1.70 H/Zr, respectively. The coefficients and standard deviations of the polynomials are given in Table 6. These standard deviations yield a probable error of $\sim 6\%$ (95% confidence limits) at reactor operating temperatures. No measurements were made for 1.81 H/Zr fuel, because the data obtained earlier⁽⁴⁾ were considered sufficiently accurate. The "best" values given in that study yield the third order polynomial shown in Figure 6d, the coefficients of which are given in Table 6. Although the standard deviation obtained from these values, 0.0005, yields a probable error of $\sim 2\%$ at reactor operating temperatures, Vetrano *et al.*⁽⁴⁾ claim an accuracy of only 5%.

1. 1.58 H/Zr

Only one specimen was measured over the entire temperature range. The second specimen gave values which were in good agreement with those of the first specimen at the higher temperatures ($\sim 860^\circ\text{C}$). During cooling, however, the back face temperature transients were observed to be anomalous. Examination of the specimen after the run revealed the presence of hairline cracks;

a. 1.58 H/Zr Fuel

c. 1.70 H/Zr Fuel

b. 1.65 H/Zr Fuel

d. 1.81 H/Zr Fuel

Figure 6. Thermal Diffusivity

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these cracks could account for the anomalous behavior. The remaining 1.58 H/Zr specimens were also found to have fine cracks, so no further measurements were made on this composition.

The results obtained in an earlier study⁽³⁾ are also given in Figure 6a. The results of the two studies agree within experimental error, over the range of 200 to 800°C. The discrepancy below this range can be attributed primarily to differences in instrumentation. In the present study, the hydrogen pressure was accurately measured and controlled; in the previous work, a sufficiently sensitive pressure sensor was not available, so that a considerable uncertainty was present in the composition at low temperatures. The difference between the high-temperature values obtained in the two studies range from 8% at 800°C to 18% at 930°C. Since the precision of the individual measurements was the same in both studies, the differences in this temperature range are difficult to resolve. The discrepancy may be due to small differences in the hydrogen content or microstructure of the fuel used in the two studies. Metallographic examination showed that the specimens used in the present work consisted of uniform equiaxed δ grains, with no indication of ϵ phase. Photomicrographs given in the report of Nakata *et al.*⁽³⁾ show a considerable amount of the banded structure found in ϵ -phase fuel. Thus, it appears that significantly more dehydriding was required in the earlier work to obtain the desired H/Zr ratio than was required in the present work.

The apparent inflection at $\sim 700^\circ\text{C}$ obtained in this work may not be real, since no phase transformation occurs at this composition in the temperature range shown.^(9,13) In this connection, it should be noted that statistically greater weight was given to the high-temperature data in the present work than in the earlier work; in the present work, 22 of the 40 data points were obtained at temperatures above 800°C, whereas only 5 of the 60 data points of the earlier work were obtained at these temperatures. The true values probably lie between the two curves, close to an extrapolation of the curve obtained in this work for the range of 0 to 700°C.

2. 1.65 H/Zr

The curve given in Figure 6b is the best fit of all the data obtained from three specimens. The individual curves (not shown) for each of the specimens were within a $\pm 2\%$ band over the entire temperature range. A clustering of

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data points occurs below the curve in the region of 200 to 250°C, and above the curve in the region of 400 to 450°C. This clustering suggests that it might be appropriate to represent the data by two nearly straight lines, intersecting in the 200 to 250°C region. Such curves would be compatible with the results of a recent phase study,⁽¹³⁾ in which a transformation from $(\delta + \epsilon)$ to ϵ phase was found to occur at 150 to 200°C. The sensitivity of thermal diffusivity measurements, however, is not sufficient to permit independent conclusions with respect to the occurrence of phase transitions. In any case, the smooth curve given is sufficiently accurate for the determination of thermal conductivity.

3. 1.70 H/Zr

The curve given in Figure 6c is the best fit of all the data obtained from three specimens. The individual curves (not shown) for each of the specimens were within a $\pm 1.5\%$ band over the entire temperature range. Again, hindsight suggests that the inflection at $\sim 500^\circ\text{C}$ may be due to the observed⁽¹³⁾ $(\delta + \epsilon)$ to δ transition at approximately this temperature.

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V. THERMAL CONDUCTIVITY

A. METHOD

Since the thermal conductivity (K) of hydrides cannot be measured directly with meaningful results, it was calculated from the relationship

$$K = \alpha c_p \rho, \quad \dots (9)$$

where α , c_p , and ρ are the thermal diffusivity, specific heat, and density.

The variations of the densities of SNAP fuel with temperature were determined from earlier thermal expansion measurements,⁽¹³⁾ obtained on compositions ranging from 1.70 to 1.81 H/Zr. Isotropic expansion was assumed, since all specimens used in both studies were polycrystalline and were subjected to high temperatures before the measurement of the pertinent thermophysical properties. Values of the ratio (R) of the density at temperature (t) to the density at 0°C were obtained from the expression

$$R = \rho_t / \rho_0 = V_0 / V_t = (\ell_0 / \ell_t)^3, \quad \dots (10)$$

where ρ is density, V is volume, ℓ is the measured length, and the subscripts refer to temperature. The ratios obtained from each composition (more than 144 values in each case) were analyzed by a polynomial least squares method. The resulting polynomials are shown in Figure 7, together with similar results obtained using the expansion coefficients of zirconium.⁽¹⁸⁾ Since the ratio at 900°C for 1.70 H/Zr is only 0.015% more than that of 1.73 H/Zr, and 0.7% less than that of zirconium, it is considered reasonable to use the expression obtained for 1.70 H/Zr for both 1.58 and 1.65 H/Zr. The error introduced into the conductivity values for the two lower compositions will thus be considerably less than 0.7%, and probably near 0.02%. The polynomials obtained for the density ratios of 1.70 and 1.81 H/Zr are given by Equations 11 and 12, respectively:

$$R = 1 - (1.78 \pm 0.15)10^{-5} t - (3.31 \pm 0.48)10^{-8} t^2 + (2.3 \pm 0.4)10^{-11} t^3, \quad \dots (11)$$

Figure 7. Density Ratios vs Temperature for SNAP Fuels

$$R = 1 - (2.06 \pm 0.02)10^{-5} t - (1.64 \pm 0.02)10^{-8} t^2 \quad \dots (12)$$

The standard deviations for these compositions were 0.00015 and 0.00009.

Since, in general, different temperatures were used for the individual measurements of enthalpy and thermal diffusivity, the calculation of thermal conductivity from experimental values of these quantities was not attempted. Instead, values of specific heat, thermal diffusivity, and density were calculated, at 10°C intervals for the required temperature ranges, from the polynomial expressions for these quantities. Thermal conductivity was then obtained at each of the temperatures, as the product of the three quantities. The resulting values were then subjected to a polynomial least squares treatment, which yielded fourth order polynomials as the best fit in each case.

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B. RESULTS AND DISCUSSION

The thermal conductivities obtained in this study are given in Figures 8a, b, c, and d, together with the results of earlier studies^(3,4) on 1.58 and 1.81 H/Zr fuel. The coefficients of the fourth order polynomials are given in Table 7, with two standard deviations. The first, labelled "Polynomial Fit," reflects the quality of the fit of the polynomial to the thermal conductivities (calculated at 10°C intervals) from which it was derived; the second, labelled "Calculated," is more realistic, and was obtained from the standard deviations of the specific heat, thermal conductivity, and density by the method described in Appendix II. The "Calculated" standard deviations yield 95% confidence limits of ~7% for all compositions at reactor operating temperatures.

The differences between the conductivities found for 1.58 H/Zr fuel in this study and those reported by Nakata et al.⁽³⁾ are due primarily to the methods used in the determination of specific heat (calorimetric, in this study, vs pulse heating, in their work). The unusual shape of the curve (Figure 8a) obtained for this composition, as compared with the curves (Figures 8b, c, and d) obtained for the other compositions, is due to two factors. First, the specific heat for 1.58 H/Zr (Figure 5a) appears to be almost a parabolic function of temperature, whereas the specific heats (Figures 5b, c, and d) found for the other compositions vary almost linearly with temperature. Secondly, the diffusivity decreases more rapidly in the low-temperature region for 1.58 H/Zr fuel than it does for the other compositions.

The differences between the conductivity values for 1.81 H/Zr (Figure 8d) obtained in this study and those given by Vetrano et al.⁽⁴⁾ are within the estimated errors of the two studies, 7 and 5%, respectively. The deviation at low temperatures is probably the result of differences in the methods used to determine specific heat. The specific heats of Vetrano et al.⁽⁴⁾ were obtained as averages of pulse heating and calorimetric data, with greater weight given to the latter. Since pulse heating yielded lower values of specific heat than the calorimetric method, lower conductivity values were obtained than would have been the case if pulse heating had not been used. Above 550°C, the pulse heating method was not used, so the influence of this method on their specific heats was less at higher temperatures than at low temperatures. Their calorimetric data, however, include only 3 data points above 462°C; whereas 13 of the 21

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TABLE 7
THERMAL CONDUCTIVITY OF SNAP FUELS
 $K(\text{cal/cm-sec-}^\circ\text{C}) = a_0 + a_1 t + a_2 t^2 + a_3 t^3 + a_4 t^4$

H/Zr	$a_0 \times 10^2$	$a_1 \times 10^5$	$-a_2 \times 10^8$	$a_3 \times 10^{10}$	$-a_4 \times 10^{14}$	Standard Deviation	
						Polynomial Fit	Calculated
1.58	4.853 ± 0.003	-6.12 ± 0.05	-9.71 ± 0.22	0.107 ± 0.035	4.41 ± 0.19	0.00007	0.002
1.65	3.9965 ± 0.0002	2.166 ± 0.003	4.43 ± 0.01	1.111 ± 0.002	8.23 ± 0.01	0.000004	0.002
1.70	3.7267 ± 0.0005	3.817 ± 0.009	7.01 ± 0.04	1.223 ± 0.007	8.31 ± 0.04	0.00001	0.002
1.81	4.971 ± 0.001	1.71 ± 0.02	6.00 ± 0.10	2.19 ± 0.02	21.2 ± 0.1	0.00002	0.002
1.81*	4.38 ± 0.02	6.25 ± 0.59	22.4 ± 0.4	5.53 ± 0.12	45.0 ± 6.9	0.0002	

*From "best" values given on page 70 of Reference 4; estimated error, 5%.

a. 1.58 H/Zr Fuel

c. 1.70 H/Zr Fuel

b. 1.65 H/Zr Fuel

d. 1.81 H/Zr Fuel

Figure 8. Thermal Conductivity

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data points of this work were obtained above this temperature. Thus, differences between the two curves at the higher temperatures is attributed to the greater statistical weight given to high-temperature data in the present study. On the basis of these considerations, it is believed that the values obtained in this study are probably more nearly correct than those of the earlier work.

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VI. SUMMARY

The thermophysical properties, at reactor operating temperatures, of four compositions of SNAP fuel are given in Tables 8 through 10. The values for 1.65 and 1.70 H/Zr have been averaged, because the values for the separate compositions differ by only 1%, in comparison to estimated errors of 4 to 8% for the three properties. The errors given in these tables correspond to 95% confidence limits (2σ) for the temperature ranges given. Additional error may be present in the values for the intermediate compositions (Table 9), since the effects of phase transformations could not be explicitly determined with the receiver of the calorimeter at room temperature.

TABLE 8
THERMOPHYSICAL PROPERTIES OF 1.58 H/Zr FUEL

Temperature (°C)	Specific Heat (cal/gm-°C) ±4.0%	Thermal Diffusivity (cm ² /sec) ±5.6%	Thermal Conductivity (cal/cm-sec-°C) ±6.6%
500	0.140	0.0483	0.0408
550	0.148	0.0469	0.0420
600	0.158	0.0457	0.0434
650	0.167	0.0446	0.0448
700	0.178	0.0435	0.0464
750	0.189	0.0424	0.0478
800	0.201	0.0411	0.0491
850	0.213	0.0396	0.0502
900	0.226	0.0378	0.0510
950	0.240	0.0357	0.0513

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TABLE 9
THERMOPHYSICAL PROPERTIES OF 1.65 AND 1.70 H/Zr FUEL

Temperature (°C)	Specific Heat (cal/gm-°C) ±3.6%	Thermal Diffusivity (cm ² /sec) ±6.8%	Thermal Conductivity (cal/cm-sec-°C) ±8%
500	0.147	0.0550	0.0486
550	0.154	0.0534	0.0494
600	0.162	0.0519	0.0503
650	0.170	0.0505	0.0510
700	0.176	0.0489	0.0516
750	0.184	0.0473	0.0518
800	0.191	0.0454	0.0516
850	0.198	0.0434	0.0510
900	0.206	0.0410	0.0499

TABLE 10
THERMOPHYSICAL PROPERTIES OF 1.81 H/Zr FUEL

Temperature (°C)	Specific Heat (cal/gm-°C) ±6%	Thermal Diffusivity (cm ² /sec) ±5%	Thermal Conductivity (cal/cm-sec-°C) ±7%
500	0.148	0.0645	0.0574
550	0.155	0.0626	0.0579
600	0.161	0.0604	0.0581
650	0.167	0.0578	0.0577
700	0.173	0.0546	0.0563
750	0.179	0.0507*	0.0539*
760	0.180	0.0498*	0.0532*

*By extrapolation of the diffusivity curve derived from the values given in Reference 4.

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APPENDIX I
ENTHALPY AND THERMAL DIFFUSIVITY DATA

TABLE 11
ENTHALPY CHANGE OF
1.58 H/Zr FUEL

Temperature (°C)	Enthalpy Change (cal/gm)
200	15.008
300	26.115
400	38.470
200	14.818
500	51.796
600	66.761
700	82.853
800	100.359
900	124.341
760	94.012
704	83.807
804	103.428
300	27.502
400	38.895
600	67.021
655	75.432
855	113.598

TABLE 12
ENTHALPY CHANGE OF
1.65 H/Zr FUEL

Temperature (°C)	Enthalpy Change (cal/gm)
93	5.864
200	15.342
260	20.706
300	24.351
400	37.979
500	51.843
600	67.280
700	85.000
800	103.932
900	121.919
149	10.538
275	23.477
300	26.902
325	28.940
350	32.341
600	67.252
650	75.224
700	83.335
800	102.929

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TABLE 13
ENTHALPY CHANGE OF
1.70 H/ Zr FUEL

Temperature (°C)	Enthalpy Change (cal/gm)
200	14.742
300	26.148
400	38.351
500	51.749
600	67.280
800	104.652
650	76.285
700	84.683
700	84.501
900	122.046

TABLE 14
ENTHALPY CHANGE OF
1.81 H/ Zr FUEL

Temperature (°C)	Enthalpy Change (cal/gm)
200	12.565
400	39.514
600	68.811
482	51.558
467	48.900
441	44.414
300	26.216
200	18.481
200	14.896
538	61.253
593	67.240
649	76.749
760	97.111
704	86.109
680	82.003
492	52.432
525	57.050
539	59.187
560	62.736
593	68.246
635	74.445

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TABLE 15
THERMAL DIFFUSIVITY OF 1.58 H/Zr FUEL

Temperature (°C)	Diffusivity (cm ² /sec)	Temperature (°C)	Diffusivity (cm ² /sec)
Sample 398-4-2-3			
886	0.0372	419	0.0520
887	0.0404	417	0.0526
888	0.0395	417	0.0516
925.5	0.0373	420	0.0526
926	0.0371	10	0.0883
926.5	0.0373	11	0.0857
924.5	0.0356	92	0.0774
922	0.0377	89	0.0743
926.5	0.0383	89	0.0754
845	0.0415	216	0.0649
847.5	0.0404	223	0.0616
845	0.0402	225	0.0606
842	0.0391	223	0.0614
684	0.0440	305	0.0557
679	0.0427	309	0.0558
676	0.0446	312	0.0568
Sample 398-4-2-1			
875	0.0385	867	0.0377
873.5	0.0381	864.5	0.0383
873	0.0372	865	0.0386
869	0.0375	866	0.0382

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TABLE 16
THERMAL DIFFUSIVITY OF 1.65 H/Zr FUEL

Temperature (°C)	Diffusivity (cm ² /sec)	Temperature (°C)	Diffusivity (cm ² /sec)
Sample 398-3-4-6			
821	0.0441	210	0.0704
822	0.0433	299	0.0649
60	0.0826	292	0.0639
228	0.0654	356	0.0607
227	0.0656	360	0.0607
26	0.0852	362	0.0611
29	0.0891	447	0.0592
28	0.0875	442	0.0603
111	0.0800	431	0.0572
113	0.0807	415	0.0592
114	0.0784	416	0.0592
54	0.0852	483	0.0565
55	0.0867	487	0.0558
55	0.0845	479	0.0572
225	0.0664	471	0.0551
Sample 398-3-4-4			
824	0.0442	155	0.0775
832.5	0.0436	173.5	0.0734
832	0.0444	241	0.0669
831	0.0440	246	0.0664
831	0.0443	338	0.0617
889	0.0405	400	0.0581
888	0.0405	404	0.0592
901	0.0407	407	0.0618
729.5	0.0501	458.5	0.0565
719	0.0488	463.5	0.0555
718	0.0494	466	0.0581
717.5	0.0493	467	0.0600
578	0.0517		
Sample 398-3-4-1			
895	0.0418	683	0.0478
897.5	0.0403	648	0.0479
898	0.0426	642	0.0496
898	0.0430	380	0.0571
865	0.0428	385	0.0575
866	0.0429	389	0.0609
865	0.0429	391	0.0579
828	0.0433	231	0.0632
826.5	0.0437	243	0.0652
826	0.0453	275	0.0617
826	0.0445	289	0.0643
826	0.0459	290	0.0656
825	0.0447	16	0.0882
789	0.0438	15	0.0882
784	0.0446	62	0.0834
782	0.0452	68	0.0849
780	0.0453	70	0.0801
780	0.0441	69	0.0857
780	0.0457	186	0.0686
748	0.0446	189	0.0686
742	0.0471	164	0.0701
739	0.0461	161	0.0712
736	0.0485	543	0.0526
735	0.0477	545	0.0523
686	0.0476	544	0.0522

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TABLE 17
THERMAL DIFFUSIVITY OF 1.70 H/Zr FUEL

Temperature (°C)	Diffusivity (cm ² /sec)	Temperature (°C)	Diffusivity (cm ² /sec)
Sample 398-2-4-6			
868	0.0438	228	0.0674
868	0.0449	233	0.0667
868	0.0436	402	0.0615
865	0.0435	395	0.0591
864	0.0420	409	0.0586
863	0.0422	419	0.0588
712	0.0476	425	0.0562
710	0.0509	436	0.0580
710	0.0473	14	0.0868
710	0.0475	44	0.0836
606	0.0527	100	0.0790
605	0.0492	113	0.0784
599	0.0526	116	0.0745
597	0.0529	308	0.0630
217	0.0672	300	0.0626
217	0.0664		
Sample 398-2-4-3			
825	0.0458	9	0.0872
826	0.0439	11	0.0888
825	0.0435	110	0.0766
824	0.0446	102	0.0779
781	0.0464	100	0.0819
776	0.0469	98	0.0783
776.5	0.0465	41	0.0867
779	0.0451	41	0.0864
350	0.0617	192	0.0694
349	0.0638	197	0.0733
347	0.0608	499	0.0573
346	0.0613	499	0.0555
346	0.0640	635	0.0523
237	0.0674	636	0.0511
235	0.0687	636	0.0532
247	0.0667	636.5	0.0510
Sample 398-2-4-2			
855.5	0.0427	267	0.0632
854	0.0419	268	0.0622
854.5	0.0425	415	0.0558
847	0.0468	428	0.0585
854.5	0.0425	433	0.0555
15	0.0879	568	0.0529
15	0.0866	573	0.0512
101.5	0.0762	576	0.0518
98	0.0760	578	0.0516
97	0.0768	580	0.0535

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APPENDIX II STATISTICAL ANALYSIS

The standard deviation (σ_y) of a polynomial is given by⁽¹⁹⁾

$$\sigma_y = \sqrt{\frac{\sum (\omega_i d_i)^2}{N - M - 1}} \quad , \quad \dots(13)$$

where the d_i are the deviations between the calculated and observed values of the dependent variable (y), the ω_i are the weighting factors for the deviations, N is the number of data points, M is the degree of the polynomial, and the summation is carried out for $i = 1$ to N . For a normal distribution, 68.3% of all observations of y will fall within the range of $Y \pm \sigma_y$, where Y is the value given by the polynomial; 95.4% of the observations will fall within the range of $Y \pm 2\sigma_y$. The standard deviations given in this report were obtained with all $\omega_i = 1$.

The standard deviations (σ_{a_i}) of the coefficients (a_i) of the polynomial are given by⁽²⁰⁾

$$\sigma_{a_i} = \sigma_y \sqrt{\frac{F_{ii}}{D}} \quad , \quad \dots(14)$$

where F_{ii} is the cofactor of the element A_{ii} in the matrix of the coefficients of the normal equations, and D is the determinant of that matrix.

Since specific heat is approximately given by $c_p = \Delta H / \Delta T$, where ΔH is the change in specific enthalpy accompanying the change in temperature (ΔT), the variance (V_c) in the specific heat at a given temperature is given by

$$V_c = \left(\frac{\sigma_c}{c_p} \right)^2 = \left(\frac{\sigma_{\Delta T}}{\Delta T} \right)^2 + \left(\frac{\sigma_{\Delta H}}{\Delta H} \right)^2 \quad . \quad \dots(15)$$

In using this expression, the values of ΔH were obtained from the polynomial expressions at the given temperature. The values of $\sigma_{\Delta H}$ were those obtained from Equation 13, and the values of $\sigma_{\Delta T}$ were assumed to be 10° for all temperature differences. The relative error in heat capacity is given by the square root of the variance, and the standard deviation can then be calculated for any

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given temperature. The values of σ_c given in the report are average values for reactor operating temperatures. The errors given in Tables 8 through 10 were obtained from the expression

$$\% \text{ Error in } c_p = 2(c_p)(\sigma_c)100 \quad , \quad \dots(16)$$

so that they correspond to the 95.4% confidence limit.

Similarly, the error in thermal diffusivity is given by the expression

$$\% \text{ Error in } \alpha = 2(\alpha)(\sigma_\alpha)100 \quad , \quad \dots(17)$$

where σ_α is the standard deviation of the polynomial expression for thermal diffusivity, and α is the average value of diffusivity in the operating temperature range. In the case of 1.81 H/Zr fuel, the error was taken to be 5%, the value given by Vetrano and his coauthors.⁽⁴⁾

The error in the thermal conductivity at any given temperature can be obtained from the square root of the variance (V_K).

$$V_K = \left(\frac{\sigma_K}{K}\right)^2 = V_c + V_{\alpha\rho} = V_c + \left(\frac{\sigma_\alpha}{\alpha}\right)^2 + \left(\frac{\sigma_\rho}{\rho}\right)^2 \quad , \quad \dots(18)$$

where the values of α , V_c , and ρ are obtained at the given temperature, and σ_α and σ_ρ are the standard deviations of diffusivity and density. Since σ_ρ/ρ is much smaller than the corresponding quantities for specific heat and thermal diffusivity (0.016% vs 2 to 3%), it was neglected in the determination of the error in thermal conductivity. This error is then given by

$$\% \text{ Error in } K = 2(V_K)^{1/2} 100 = 200(V_c + V_\alpha)^{1/2} \quad . \quad \dots(19)$$

The standard deviations obtained from the polynomial expressions for thermal conductivity are not used. The values given in Table 7 as calculated standard deviations were obtained from the expression

$$\sigma_K = K(V_K)^{1/2} \quad , \quad \dots(20)$$

where V_K is obtained from Equation 18 at operating temperatures, and K is obtained from the polynomial expressions for thermal conductivity at the same temperatures.

APPENDIX III

THEORETICAL HEAT CAPACITY

The theoretical model used in this work was developed by Rhoades,⁽¹⁴⁾ and is based on a suggestion by Kittel⁽²¹⁾ that the heat capacity of a diatomic lattice can be approximated by the sum of the heat capacities of the two components, provided the atomic mass ratio is far from unity; the heat capacity of the lighter atom is determined, using the Einstein model, and that of the heavier atom is determined, using the Debye model. In this way, Rhoades found that the heat capacity (per gram atom of zirconium) of SNAP fuel can be expressed as

$$C_p = C_D + xC_E + (K + L + C)T + B \quad , \quad \dots(21)$$

where x is the H/Zr atom ratio, K is the " $C_p - C_v$ " coefficient, L is the electronic heat capacity, T is absolute temperature, $B + CT$ represents the heat capacity of uranium, and C_D and C_E are the Debye and Einstein heat capacities (constant volume) of zirconium and hydrogen, respectively.

The treatment used in the present work differs from that of Rhoades, who assumed that the Debye temperature of pure zirconium (270°K) is applicable to all fuel compositions, and that the Einstein temperature would be constant. Since both the Debye and Einstein temperatures are related to lattice vibrations, they would be expected to vary with crystal structure. Hence, since the crystal structure of SNAP fuel varies with hydrogen content, these characteristic temperatures should be expected to depend on composition. In order to determine these temperatures and the sum of the $C_p - C_v$ coefficient and electronic heat capacity for each composition, an iterative least squares computer program was developed, based on the method described by Young.⁽²²⁾ For each composition, the data to which the theoretical heat capacity was to be fit consisted of values of heat capacity calculated at 50° intervals, using the polynomials given in Table 4. These data were fit to the expression

$$C_p = C_D + xC_E + yC_U + AT \quad , \quad \dots(22)$$

where y is the U/Zr atom ratio, A is the sum of $K + L$, and C_U , the molar heat capacity of uranium, is given by⁽²³⁾

$$C_U = -4.1635 + 0.03705T - 1.237 \times 10^{-5}T^2 + 338630/T^2 \quad . \quad \dots(23)$$

The Debye heat capacity (C_D) is given by^(24, 25)

$$C_D = 3R \left[1 - \frac{(\theta_D/T)^2}{20} + \frac{(\theta_D/T)^4}{560} - \frac{(\theta_D/T)^6}{18144} \right], \quad \dots(24)$$

and the Einstein heat capacity (C_E) is given by⁽²⁶⁾

$$C_E = \frac{3R(\theta_E/T)^2}{4 \sinh^2(\theta_E/2T)} \quad \dots(25)$$

The effect of phase transformations in the uranium was neglected, since, even at the maximum temperature (950°C), the use of Equation 22 leads to an error of <0.4% in the theoretical value of the heat capacity of fuel.

Values of θ_D , θ_E , and A were obtained such that, for each composition, the difference between the theoretical and polynomial value did not exceed ~10% of the latter at any temperature within the range of validity of the polynomial (see Figures 9a, b, c, and d). The values of the three parameters and the root mean square (rms) deviation between the theoretical and polynomial values are given in Table 18 for each composition. The Einstein temperature is found to decrease with increasing hydrogen content, in agreement with the observation that the free energy of formation of the fuel also decreases with increasing hydrogen content. The Debye temperatures obtained for the three higher H/Zr ratios appear to be very reasonable; while that obtained for 1.58 H/Zr is lower than would be expected, in comparison with those given for the other three compositions. This discrepancy may be related to phase transformations described in

TABLE 18
PARAMETERS FOR THEORETICAL HEAT CAPACITY*

Hydrogen Content (H/Zr)	θ_E (°K)	θ_D (°K)	A (cal/mole-°K ²)	rms Deviation (cal/mole-°F)	Range (°C)
1.58	3434	141	8.97×10^{-3}	0.94	0 - 950
1.65	2794	220	7.28×10^{-3}	0.39	0 - 950
1.70	2590	244	6.48×10^{-3}	0.27	0 - 900
1.81	2480	369	5.52×10^{-3}	0.39	0 - 750

*For use with Equation 22 to obtain C_p in cal/gm atom of Zr - °K

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a. 1.58 H/Zr Fuel

1-22-68 UNCL

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b. 1.65 H/Zr Fuel

1-22-68 UNCL

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c. 1.70 H/Zr Fuel

d. 1.81 H/Zr Fuel

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Figure 9. Theoretical Heat Capacity

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the next paragraph. The values of A are 2 to 3 times greater than the values obtained by Rhoades.⁽¹⁴⁾ The trend in these values may not be real, since the term is essentially a "catchall" term in the least squares treatment and, in any case, contributes <5% to the theoretical heat capacity, even for 1.58 H/Zr at 950°C.

Figures 9b, c, and d show that the agreement between the theoretical and polynomial heat capacities is reasonably good for the three higher H/Zr ratios. In the case of 1.58 H/Zr fuel, however, the agreement (Figure 9a) is poor. Very recent⁽²⁸⁾ studies of the $(\alpha + \delta) \rightleftharpoons \delta$ boundary in SNAP fuel indicate that 1.58 H/Zr fuel may be in the two-phase $(\alpha + \delta)$ region below $\sim 100^\circ\text{C}$. If this is the case, the polynomial expression for the heat capacity may be in error, since the heat of transformation from δ (fcc) to α (hcp) may be a significant fraction of the enthalpy changes observed for this composition.

It should be noted that the theoretical model used is an approximation, and may not be an adequate description of the heat capacity for substances with the wide range of stoichiometry found in metal hydrides. A more accurate model probably can be developed by considering the effects of the interactions of vacancies and interstitials, such as was done by Libowitz⁽²⁸⁾ in his discussion of the dissociation pressures of hydrides.

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