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HEAT CAPACITY STUDIES OF
URANIUM AND URANIUM-FISSIUM ALLOYS

by

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	5
I. INTRODUCTION	5
II. MATERIALS.	6
III. APPARATUS AND METHODS	7
IV. EXPERIMENTAL RESULTS	15
V. DISCUSSION.	20
VI. CONCLUSIONS	23
VII. REFERENCES	24
APPENDIX	26

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Ice Calorimeter for Heat-Capacity Determinations.	9
2.	Ice Calorimeter.	11
3.	Diphenyl Ether Calorimeter.	12
4.	Constant-heating-rate Specific Heat Apparatus	14
5.	Heat Content of Uranium	18
6.	Heat Content of Uranium-3 w/o Fissium Alloy.	19
7.	Heat Content of Uranium-5 w/o Fissium Alloy.	19
8.	Heat Content of Uranium-8 w/o Fissium Alloy.	19
9.	Heat of Fusion vs. Gram Equivalent Weights	22

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Composition of Uranium-Fissium Alloys	6
II.	Composition of High-purity Uranium	6
III.	Heat Treatments of Heat Capacity Specimens	7
IV.	Heat Content above 0°C of Uranium	16
V.	Heat Content above 0°C of Uranium-3% Fissium Alloy.	16
VI.	Heat Content above 0°C of Uranium-5% Fissium Alloy.	17
VII.	Heat Content above 0°C of Uranium-8% Fissium Alloy.	17
VIII.	Some Comparative Values of Transition Heats of Uranium.	22

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ABSTRACT

The heat contents of high-purity uranium and uranium-fissium alloys containing 3, 5, and 8 w/o fissium were measured at temperatures from 0°C through their fusion temperatures. The total heat content above 0°C was determined by drop calorimetry and quantitative differential thermal analysis.

The total heat content from 0°C to 1200°C was found to be 16.1 ± 0.3 , 16.3 ± 0.6 , 16.3 ± 0.6 , and 16.4 ± 0.4 kcal per equivalent gram atom, for the 0, 3, 5, and 8 w/o fissium alloys, respectively. Curves of the heat content versus temperature are plotted for all the alloys and the high-purity uranium. Heats of transition and of fusion were determined. The directly measured value of 2.9 ± 0.1 kcal/g-atom for the heat of fusion of uranium is consistent with that of the alloys.

I. INTRODUCTION

This study of the heat content of uranium-fissium alloys* was made to aid in the safety evaluation of an inadvertent reactor runaway and other non-steady-state heat problems of the first fuel loading of the Experimental Breeder Reactor No. II (EBR-II).^(1,2) Also, uranium heat content data are needed for similar reactor problems and for thermodynamic applications.

Experimentally determined values for the high-temperature heat content of uranium-fissium alloys have not previously been available in the literature. Data are available for the heat content of uranium,⁽³⁻⁶⁾ but no direct measurement of the heat of fusion of uranium has been made.

This study was undertaken to determine the total heat content, including heats of transformation and fusion, of uranium and uranium-fissium alloys with fissium contents of 3, 5, and 8 w/o up to temperatures above the melting range. The data were obtained by the University of Denver, Denver Research Institute, under subcontract No. 31-109-38-1222 to Argonne National Laboratory.

*See Sec. II, p. 6 for explanation of "fissium."

II. MATERIALS

Specimens of uranium and artificial uranium-fissium alloys were made at Argonne National Laboratory. Fissium is an equilibrium concentration of fission product elements left by the pyrometallurgical reprocessing cycle designed for EBR-II. This accumulation of metals is composed of molybdenum, ruthenium, rhodium, palladium, zirconium, niobium, and technetium in relatively fixed proportions. Technetium is not included in the artificial alloys because of its scarcity and alpha activity. The phase relationships and physical properties of the simulated alloys are assumed to be not grossly different from those of the actual fission-produced alloys.^(7,8)

The compositions of the alloys and of pure uranium are shown in Tables I and II. Purity of the elements for the alloys was 99.98% for the uranium and 99.85% for the fissium.

Table I

COMPOSITION OF URANIUM-FISSIUM ALLOYS

Element	U-3 Percent Fs		U-5 Percent Fs		U-8 Percent Fs	
	w/o	Ratio X ^g /Mo ^g	w/o	Ratio X ^g /Mo ^g	w/o	Ratio X ^g /Mo ^g
Mo	1.5	1.0	2.1	1.0	3.7	1.0
Ru	1.2	0.8	1.9	0.9	3.2	0.86
Rh	0.16	0.11	0.19	0.09	0.41	0.11
Pd	0.12	0.08	0.14	0.07	0.28	0.075
Zr	0.04	0.027	0.05	0.024	0.07	0.019
Nb	0.006	0.004	0.01	0.005	0.02	0.005
Total Fs	3.03	-	4.39	-	7.68	-
U	Bal	-	Bal	-	Bal	-

Table II

COMPOSITION OF HIGH-PURITY URANIUM

Element	ppm	Element	ppm	Element	ppm	Element	ppm
C	28-29	As	<10	Fe	< 2	Ni	< 5
N	15	B	< 0.1	K	< 50	P	< 50
O	26-72	Be	< 0.1	Li	< 1	Pb	< 1
Cu	1	Bi	< 1	Mg	< 2	Sb	< 1
Si	10	Ca	< 20	Mn	< 1	Sn	< 5
Ag	< 1	Co	< 5	Mo	< 20	Ti	< 50
Al	< 5	Cr	< 1	Na	< 10	Zn	< 50

The alloy ingots were prepared by vacuum melting and casting, followed by homogenizing in the upper gamma-temperature region and quenching in water. Specimens for non-steady-state measurements and drop calorimetry were cut and machined from the homogenized ingots. The specimens for drop calorimetry were in the form of cylinders, $\frac{3}{8}$ in. in diameter by 1 in. long, and those for the non-steady-state determinations were $\frac{3}{4}$ in. in diameter and $1\frac{1}{2}$ in. long. Based on the work of Nevitt and Ziegler,⁽⁸⁾ additional vacuum heat treatments as shown in Table III were applied to some of the specimens to produce equilibrium or metastable structures for the beginning of the calorimetry.

Table III

HEAT TREATMENTS OF HEAT CAPACITY SPECIMENS

Material	Specimen	Structure	Heat Treatment
U	-	α	As cold rolled.
U + 3% Fs	A	$\alpha + \delta + \text{U}_2\text{Ru}$	25 hr at 825°C water quench. 5 hr at 525°C.
U + 3% Fs	B	γ	25 hr at 825°C, water quench.
U + 5% Fs	A	$\alpha + \delta + \text{U}_2\text{Ru}$	25 hr at 825°C, water quench. 5 hr at 525°C
U + 5% Fs	B	γ	25 hr at 825°C, water quench.
U + 8% Fs	A	$\alpha + \delta + \text{U}_2\text{Ru}$	25 hr at 825°C, water quench. 45 hr at 525°C.
U + 8% Fs	B	γ	25 hr at 825°C, water quench

A portion of the high-purity uranium bar was cold reduced and cut into the same sizes of specimens as the alloys. Heat treatments were not made until the specimens were in the calorimeter, where cold work was annealed out prior to dropping.

III. APPARATUS AND METHODS

Heat-capacity measurements were made in two calorimeters available in the laboratories of the University of Denver Research Institute. Each calorimeter consists of two main parts: the furnace, in which the

specimen is heated to a measured temperature; and a Bunsen calorimeter, which connects directly beneath the furnace. The specimen is dropped from the furnace into the calorimeter, which measures the total heat content of the specimen above the calorimeter temperature.

The ice calorimeter assembly shown in Figure 1 is capable of operating up to about 1550°C. The furnace has a molybdenum heater in the form of a helix laid in a spiral groove in an aluminum oxide core. Molybdenum and stainless steel radiation shields are used around the outside of the heater to reduce the heat losses. The inside diameter of the alumina core is $1\frac{1}{4}$ in., and the heater has a total length of slightly less than 12 in. The greatest deviation from an isothermal condition along the length of the specimen reached by this arrangement is 7°C.

In normal practice the furnace and calorimeter are operated in argon at a total pressure of about 10 mm. The pressure range is low enough to prevent excessive heat losses from the furnace elements because of convection and conduction, but is sufficient to promote equilibrium in the calorimeter in a reasonable length of time.

The temperature of the furnace is determined by controlled power input regulated by a feedback circuit and a saturable core reactor. The temperature in the furnace is sensed by four platinum/platinum-rhodium thermocouples spaced in the region where the test specimen hangs.

The specimens for drop calorimetry are hung in the furnace by means of a fine tungsten or molybdenum wire. This wire extends upward through the furnace top to a steel slug contained in a one-inch brass telescope tube. Surrounding this tube is a 3-in. telescope tube, which can be seen extending upward from the apparatus in Figure 1. A ring magnet with a leather diaphragm fits snugly between these two tubes. Upon release, the ring magnet falls and carries the steel slug with it, allowing the specimen to drop into the calorimeter well. The magnet falls freely in the first half of the tube, and in the second half the specimen is brought to a rather gentle stop by means of holes of decreasing size provided in the walls of the outer tube, so that an air damper results. After the run has been completed, it is then possible to pull the ring magnet and specimen back up so that the specimen is drawn into the furnace for an additional drop. It is found with this system at temperatures above the recrystallization temperature of the wire and with heavy specimens that an appreciable amount of breakage of the support wire occurs. In this contingency it is necessary to cool the furnace, retrieve the specimen and assemble another support wire.

Solid specimens are supported from the suspension wire in a loose basket of molybdenum or tungsten wire. The samples of liquid uranium used in this program were contained in an yttrium capsule machined from

Figure 1. Ice Calorimeter for Heat Capacity Determinations

extruded rod. Yttrium has been reported as a good metal container for molten uranium.⁽⁹⁾ These yttrium capsules were made with a thin wall and an inside diameter which barely cleared the solid uranium specimen. A thin screw cap was provided on the top to prevent splashing of the liquid material upon dropping. In some instances, the weight of the heavy uranium specimen sheared the bottom from the yttrium capsules. In only one instance was any difficulty encountered with reaction between the molten uranium and the yttrium capsule. This was with a specimen of pure uranium which had been heated in the temperature range of about 1250°C. The uranium apparently wetted the yttrium, and two holes developed in the sides of the crucible, allowing the liquid uranium to spill out. Wetting of the surface is hypothesized inasmuch as small drops of the uranium were retained on the outside of the capsule after freezing. Some difficulty was also encountered in this temperature range due to an apparent reaction between the yttrium and the molybdenum support wires. This interaction is surprising because the temperature involved is considerably below the reported eutectic temperature between yttrium and molybdenum, yet the appearance was that of a slight molten zone.

After a specimen has been heated to the desired temperature, it is dropped from the furnace into the calorimeter. Basically, the ice calorimeter consists of a tube or well of metal closed at one end, on the outside of which a layer of ice has been frozen. Its use is based on the reversible change of density which occurs when water freezes or ice melts. The mantle of ice and the water which surrounds it are confined within a fixed volume formed by a glass jar, the outer wall of the calorimeter well, and a cap for sealing the jar to the calorimeter. The design of the calorimeter used is shown in Figure 2. The ice-water system communicates with the atmosphere by means of a mercury-filled tube connected to a mercury accounting system. Thus, any addition of heat to or withdrawal of heat from the ice-water system results in a displacement of mercury. When a heated specimen enters the calorimeter, a part of the ice mantle is melted and a corresponding quantity of mercury is pulled into the system. This quantity, with suitable corrections, is a measure of the heat content of the specimen above the ice point. The amount of mercury is measured by a combined weighing and capillary displacement method. The accuracy is greatest with no corrections; the heat exchange with the surroundings is minimized by enclosing the entire calorimeter in a bath of ice and water.

Another calorimeter was used for a few of the drops made in this experimental program. The same general principle is involved, but there are some differences in the equipment, as illustrated in Figure 3. An evacuated quartz tube contains the specimen in the hot zone of a standard tube furnace capable of operation up to 1100°C. A heavy tube of stainless steel is positioned inside the furnace tube and around the quartz to insure more uniform temperature distribution. The specimen is suspended by nichrome wires which can be burned off with a pulse of electricity to allow the sample to fall freely into the calorimeter.

Figure 2. Ice Calorimeter

Figure 3. Diphenyl Ether Calorimeter

In the calorimeter the specimen is caught in a copper-mesh basket so that it does not touch the calorimeter walls. The calorimetric medium used is diphenyl ether, which contracts on melting, has a melting temperature of about 26°C , and has about three times the volume change per calorie than does water. The mercury displacement in this system is determined by means of the change in position of the mercury column in a calibrated capillary tube.

A sample calculation showing the conversion of the displaced medium to enthalpy is given in the Appendix.

In both of the calorimeters the chief sources of error include the determination of the specimen temperature, heat loss during the drop, and application of heat-leak corrections. Occasionally, inconsistencies in the data will occur when the specimen swings against the walls on the way down, or air is accidentally introduced into the mercury accounting system. Both of these sources are quite obvious and definitely point out questionable data which can be discarded. The largest single error is due to the inability to determine accurately the specimen temperature. The temperature-measuring thermocouples are not actually in contact with the specimen, but are in the furnace in a region very close to the specimen. It must then be assumed that the specimen will reach the temperature of the surrounding furnace. This assumption may lead to calculated data that are slightly low because of heat losses from the specimen into the cooler regions at the ends of the furnace. Calibrations have been made with synthetic sapphire, however, and it was found that consistent data could be obtained within about 2 percent of the values reported by the National Bureau of Standards. The errors introduced by variations in the drop loss and heat-leak corrections occur in a random manner and will tend to disappear as fitting of curves is made to the experimental points.

A third apparatus was employed to obtain the heats of transformation in the uranium-fissium system. Since these reactions did not proceed to completion in the drop calorimeters, their heat effects were not recorded. The heat content of the high-temperature phase above the calorimeter temperature was obtained. The alternative method used a thermal analysis apparatus which provided data such that the specific heat of the specimen could be calculated from a known rate of temperature rise and heat input. The apparatus is similar in many respects to that described by C. S. Smith⁽¹⁰⁾ and one constructed by J. A. Rea.⁽¹¹⁾ A special furnace with a very rapid heating rate is used with a special insulating crucible containing the experimental material or a standard material. A cross-section of the furnace used for these determinations is shown in Figure 4. The furnace consists of an alundum core, of $2\frac{1}{4}$ -in. ID and 10 in. long. Another core of 12-in. length, surrounds this. Two heater windings are used so that a rapid and closely controlled rate of heating can be provided without using an extremely high watt density on the wires. Both cores are wound with Kanthal wire, and Variacs are used to control the voltages imposed on the heaters. The temperature differential across the crucible wall controls the power delivered to the inner heater.

Figure 4
Constant-heating-rate Specific
Heat Apparatus

A differential thermocouple is placed with one bead on the inside and one bead on the outside of the crucible. This temperature difference is maintained at a constant value throughout an experimental run. Both this and the thermocouples for measurement of specimen temperatures are Chromel-Alumel. A container surrounds the entire apparatus so that the enclosure can be partially evacuated and refilled with an atmosphere of purified argon. A series of purges establishes a protective atmosphere, and zirconium in the furnace chamber cleans up residual contamination.

To obtain the specific heat of the material, it is first necessary to calibrate the apparatus for heat input at various temperatures. A heating run is made with all components in place except for the experimental material, and the time-temperature curve for the furnace is obtained to determine the amount of heat absorbed by the crucible and the other components. A second run is made with a material of a known specific heat in place of the experimental sample. The heat flux through the crucible wall can be determined from the experimentally determined rate of heating. With the knowledge of this heat flux and the rate of heating obtained with the experimental material, it is possible to calculate a specific heat or heat content of the specimens.

The standard material used for comparison in this work was OFHC copper. Both Smith and Rea used copper as the standard, and both used the value in the Metals Handbook.⁽¹²⁾ A check of this value against other values

available in the literature showed some differences among the data recorded. For the purposes of this work, the value for copper in the Metals Handbook was used in the temperature range from room temperature to about 100°C. Above 100°C the specific heat used was computed by the equation $C_p = 5.40 + 1.40 \times 10^{-3}T$ in cal/mole-°C. This is the value reported by Smithells(13) with a reported accuracy of $\pm 1\%$

In the operation of the specific heat apparatus with a material showing a phase transformation, a peak occurs in the curve of specific heat versus temperature. By integrating the area under this peak, an approximate value for the heat of transformation can be obtained. A simple calculation illustrating the method employed is shown in the Appendix. It has been found in the operation of the apparatus that the measured temperature of the peak occurs at some value below the actual transformation temperature, indicating that a thermal lag exists between the outside of the test specimen and the measuring thermocouple located in the center. The lag between the specimen itself and the thermocouple junction magnifies this displacement. This is particularly troublesome when two reactions studied are occurring over a narrow temperature range. In this situation the heat effects attributable to the various transformations cannot be obtained

IV. EXPERIMENTAL RESULTS

The data for the heat content above 0°C of all materials tested are presented in Tables IV through VII, and are presented graphically in Figures 5 through 8. The unsmoothed data for the uranium are included. The heats of transformation and fusion are also tabulated. The reaction temperatures noted are those found in the literature rather than those determined in this study(8,14) (see Table VIII for the uranium and Ref. 8 for the fissium). The units for the uranium data are given both in cal/g and kcal/g. To obtain kilocalories per equivalent gram-atom of the fissium alloys, the given units are multiplied by the equivalent gram-atomic weight and divided by 1000.

The heat content of the uranium-fissium alloys is difficult to obtain by the methods available because of the sluggishness of transformations. Upon quenching the heated specimens, the high-temperature phases are retained. Thus, we obtain the heat content of that phase above the calorimeter temperature with no indication of the magnitude of the heat of reaction. In order to obtain reaction heats by drop calorimetry, the reaction must go to completion upon relatively rapid cooling.

Table IV
HEAT CONTENT ABOVE 0°C OF URANIUM

Temperature		Heat Content			Temperature		Heat Content		
Observed (°C)	Calculated (°C)	Observed (cal/g)	Calculated		Observed (°C)	Calculated (°C)	Observed (cal/g)	Calculated	
			(cal/g)	(kcal/g-atom)				(cal/g)	(kcal/g-atom)
	0		0	0		774.6 (β)		31.6 ± 0.4	7.5 ± 0.1
140		3.01				774.6 (γ)		36.2 ± 0.5	8.6 ± 0.1
160		4.34				800		37.7 ± 0.5	9.0 ± 0.1
199		5.42			803		37.34		
	200		5.3 ± 0.1	1.26 ± 0.04	812		38.00		
221		6.18			812		38.02		
239		6.69			865		39.92		
	300		8.7 ± 0.2	2.07 ± 0.04	869		40.75		
304		9.11			883		41.20		
348		10.45				900		42.3 ± 0.5	10.1 ± 0.1
	400		12.6 ± 0.2	3.10 ± 0.04	903		42.89		
403		13.04			978		45.49		
421		13.39			990		46.51		
	500		16.7 ± 0.2	3.97 ± 0.04		1000		46.9 ± 0.5	11.2 ± 0.1
502		16.69			1088		51.0		
518		17.70			1095		51.8		
522		17.73			1100		51.3		
599		20.72				1100		51.5 ± 0.5	12.3 ± 0.1
	600		21.0 ± 0.2	5.00 ± 0.04		1132 (γ)		53.0 ± 0.6	12.6 ± 0.1
618		21.60				1132 (Liquid)		65.2 ± 0.9	15.5 ± 0.2
619		21.82			1138		60.3		
640		23.17			1140		64.7		
642		22.68			1144		65.2		
	667.4 (α)		23.4 ± 0.2	5.57 ± 0.04	1162		65.8		
	667.4 (β)		26.7 ± 0.3	6.35 ± 0.07	1181		65.4		
669		25.85				1200		67.6 ± 1.2	16.1 ± 0.3
680		27.02							
700		28.44							
	700		28.4 ± 0.3	6.76 ± 0.07					
709		28.27							
719		28.78							
742		29.92							
750		30.49							
754		31.00							

Heat of transformation $\alpha \leftrightarrow \beta$ at 667.4°C, 3.3 ± 0.5 cal/g = 0.78 ± 0.12 kcal/g-atom

Heat of transformation $\beta \leftrightarrow \gamma$ at 774.6°C, 4.6 ± 0.9 cal/g = 1.1 ± 0.2 kcal/g-atom

Heat of fusion at 1132°C, 12.2 ± 0.3 cal/g = 2.9 ± 0.3 kcal/g-atom

No simple equation fits the data from 0°C to 662°C

$$H_{774.6} - H_{667.4} = 0.0445 T(^{\circ}\text{C}) - 2.8 \text{ cal/g}$$

$$H_{1132} - H_{774.6} = 0.0465 T(^{\circ}\text{C}) + 0.3 \text{ cal/g}$$

Table V
HEAT CONTENT ABOVE 0°C OF URANIUM-3% FISSION ALLOY (cal/g)

Temp (°C)	Phases			
	$\alpha + \delta + \text{U}_2\text{Ru}$	$\alpha + \gamma + \text{U}_2\text{Ru}$	γ	Equilibrium
0	0	0	0	0
200	5.3 ± 0.1	5.7 ± 0.1	-	5.3 ± 0.1
300	8.5 ± 0.1	9.1 ± 0.1	-	8.5 ± 0.1
400	11.8 ± 0.2	12.9 ± 0.1	-	11.8 ± 0.2
500	16.0 ± 0.2	17.1 ± 0.2	-	16.0 ± 0.2
560	18.3 ± 0.2	-	-	18.3 ± 0.2
560	-	-	-	21.3 ± 0.7
600	-	21.5 ± 0.2	-	24.0 ± 0.7
640*	-	-	-	26.5 ± 0.1
690*	-	-	-	31.8 ± 1.7
700	-	-	26.3 ± 0.8	33.3 ± 2.1
800	-	-	31.3 ± 0.8	38.3 ± 2.3
900	-	-	36.3 ± 0.8	43.3 ± 2.3
1000	-	-	41.2 ± 0.8	48.2 ± 2.4
1060	-	-	44.0 ± 1.0	51.0 ± 2.5
1120	-	-	-	68.2 ± 2.5
1200	-	-	-	70.8 ± 2.9

Heat of Transformation $\alpha + \delta + \text{U}_2\text{Ru} \leftrightarrow \alpha + \gamma + \text{U}_2\text{Ru}$ at 560°C, 3.0 ± 0.5 cal/g.

Total Heat Effect 640 to 690°C, 5.3 ± 1.0 cal/g.

Total Heat Effect, 1060 to 1120°C, 17.2 ± 5.0 cal/g.

Equivalent gram-atom: 230.51 g.

*This temperature region contains two- and three-phase mixtures with varying proportions of the phases. The experimental technique was incapable of defining the details of the heat effects.

Table VI
HEAT CONTENT ABOVE 0°C OF URANIUM-5%
FISSIUM ALLOY (cal/g)

Temp (°C)	Phases			
	$\alpha + \beta + \text{U}_2\text{Ru}$	$\alpha + \gamma + \text{U}_2\text{Ru}$	γ and $\gamma + \text{U}_2\text{Ru}$	Equilibrium
0	0	0	0	0
200	5.3 ± 0.1	5.8 ± 0.1	5.8 ± 0.1	5.3 ± 0.1
300	8.3 ± 0.1	9.3 ± 0.1	9.3 ± 0.2	8.3 ± 0.1
400	11.4 ± 0.2	13.0 ± 0.2	13.0 ± 0.2	11.4 ± 0.2
500	15.6 ± 0.2	17.4 ± 0.2	17.4 ± 0.3	15.6 ± 0.2
560	18.0 ± 0.2	-	-	18.0 ± 0.2
560	-	-	-	20.8 ± 0.6
600	-	22.0 ± 0.3	22.0 ± 0.3	23.1 ± 0.7
640	-	-	-	25.3 ± 0.7
640	-	-	-	27.3 ± 0.7
700	-	-	26.7 ± 0.5	31.1 ± 1.5
750	-	-	-	36.0 ± 1.5
800	-	-	31.8 ± 0.4	38.6 ± 1.6
900	-	-	36.9 ± 0.5	43.7 ± 1.7
1000	-	-	42.0 ± 0.5	48.8 ± 1.7
1010	-	-	-	49.3 ± 1.7
1100	-	-	-	68.8 ± 2.3
1180	-	-	-	71.4 ± 2.5

Heat of Transformation $\alpha + \beta + \text{U}_2\text{Ru} \leftrightarrow \alpha + \gamma + \text{U}_2\text{Ru}$ at 560°C, 2.8 ± 0.4 cal/g.

Heat of Transformation $\alpha + \gamma + \text{U}_2\text{Ru} \leftrightarrow \gamma + \text{U}_2\text{Ru}$ at 630°C, 2.0 ± 0.4 cal/g.

Heat Effect $\gamma + \text{U}_2\text{Ru} = \gamma$ at about 700 to 740°C, 3.6 ± 0.4 cal/g.

Total Heat Effect 1010 to 1100°C, 19.5 ± 4.0 cal/g

Equivalent gram-atom: 224.24 g.

Table VII
HEAT CONTENT ABOVE 0°C OF URANIUM-8% FISSIUM ALLOY (cal/g)

Temp (°C)	Phases				Equilibrium
	$\alpha + \beta + \text{U}_2\text{Ru}$	$\alpha + \gamma + \text{U}_2\text{Ru}$	$\gamma + \text{U}_2\text{Ru}$	γ	
0	0	0	0	0	0
200	5.3 ± 0.1	6.1 ± 0.1	6.1 ± 0.1	-	5.3 ± 0.1
300	8.4 ± 0.1	9.8 ± 0.1	9.8 ± 0.1	-	8.4 ± 0.1
400	11.6 ± 0.2	13.5 ± 0.2	13.5 ± 0.2	-	11.6 ± 0.2
500	15.9 ± 0.2	18.0 ± 0.3	-	-	15.9 ± 0.2
560	19.3 ± 0.2	-	-	-	19.3 ± 0.2
560	-	-	-	-	22.3 ± 0.8
600	-	22.2 ± 0.3	-	-	25.2 ± 0.9
700	-	-	29.0 ± 0.4	-	32.0 ± 0.9
800	-	-	35.8 ± 0.5	-	38.8 ± 1.0*
900	-	-	-	42.0 ± 0.5	45.0 ± 1.0*
950	-	-	-	44.7 ± 0.6	47.7 ± 1.1
1000	-	-	-	-	58.0 ± 2.5
1060	-	-	-	-	70.0 ± 1.8
1150	-	-	-	-	73.0 ± 1.9

Heat of transformation $\alpha + \beta + \text{U}_2\text{Ru} \leftrightarrow \alpha + \gamma + \text{U}_2\text{Ru}$ at 560°C, 3.0 ± 0.5 cal/g.

Total heat effect, 950 to 1060°C, 22.3 ± 2.9 cal/g.

Equivalent gram-atom: 214.92 g.

*There is a distinct change in slope in the curve at about 860°C. This probably corresponds to the disappearance of U_2Ru as a separate phase, but appears about 50°C higher than expected.

Figure 5. Heat Content of Uranium

Figure 6. Heat Content of Uranium-3 w/o Fissium Alloy

Figure 7. Heat Content of Uranium-5 w/o Fissium Alloy

Figure 8. Heat Content of Uranium-8 w/o Fissium Alloy

Data on heat of transformation were obtained by the non-steady-state measurements previously described. Lack of refinement in our apparatus results in data of lower accuracy than obtainable by drop

calorimetric methods. The specimens used were stabilized in the $\alpha + \delta + \text{U}_2\text{Ru}$ region. Upon heating these specimens, transformations occurred, accompanied by resultant heat effects. In all three of the fissium alloys a clear reaction was observable at the boundary between the $\alpha + \delta + \text{U}_2\text{Ru}$ and $\alpha + \gamma + \text{U}_2\text{Ru}$ regions. In the other reactions, however, the transformation appeared to occur over a range of temperatures rather than at any discrete values. In the 3 percent alloy, a substantial heat effect was noted from about 630 to 670°C. It was impossible to distinguish the various reactions which were occurring in this material. In the 5 percent alloy, there was apparently enough sluggishness in the transformation occurring that some indication of location of the heat effect could be made as well as a determination of its magnitude. We were unable, however, to distinguish any significant breaks in the data for the 8 percent alloy above the first transformation by the non-steady-state technique.

Heat content data were obtained for the low-temperature equilibrium structures of $\alpha + \delta + \text{U}_2\text{Ru}$ by drop calorimetry up to the transformation temperature. Half of the specimens were stabilized in the $\alpha + \gamma + \text{U}_2\text{Ru}$ region, and heat contents of these specimens were obtained from the calorimeter temperature up to their upper temperature of stability.

The total heat content data presented for the fissium alloys includes a constructed equilibrium curve for heat content as a function of temperature. This curve shows the heat required to transfer a stabilized specimen at one temperature to a stabilized specimen at another on the curve.

V. DISCUSSION

The alloy materials used herein correspond to those investigated by Nevitt and Zegler,^(8,15) and their nomenclature for the phases has been adopted. The phase relationships expressed by them have also been accepted. Error in the temperature measurements in the furnace and deviation from equilibrium structures can account for the difference in transformation temperatures from those reported by Nevitt and Zegler. The specimens used for heat content measurements were probably all at, or nearly at, equilibrium in the furnace, but the unknown cooling rate after dropping into the calorimeter could produce nonequilibrium structures of unknown composition. Some evidence of this was seen in the experimental runs, particularly for the 3 percent fissium alloy.

The tabular data include an estimation of the uncertainty of each value. These uncertainties cumulate the sources of error existing in the system and the techniques of measurement. The corrections and assumptions of temperature equilibrium are a more significant portion of the total heat content at lower temperatures, and the uncertainty below 400°C is only

an indication of consistency rather than absolute accuracy. These data are probably lower than the actual values, but by an indeterminate amount. The most serious source of error is the determination of the specimen temperature. The heat loss during the drop, and application of heat leak corrections and the temperature drift in the furnace also contribute.

The heat content of the $\alpha + \delta + \text{U}_2\text{Ru}$ materials is lower than would be expected for the alloys involved. This is most marked in the 3 and 5 percent fissium alloys. The heat content decreases with increasing fissium content, reaching a minimum value somewhere around the 5 percent alloy and increases with additional fissium to the 8 percent alloy. The $\alpha + \gamma + \text{U}_2\text{Ru}$ specimens and those dropped from higher temperatures gave heat contents that increased with increasing fissium content. This is the type of variation from the heat content of pure uranium that would be expected from the addition of these alloying elements.

It is only with great caution that one can predict the variation of heat content with changes in alloy composition. This is particularly true when compounds may be formed in the system, and when multiple phase relationships are involved. Estimations of this sort are also useful only up to the temperature where a first transformation may occur. Kubaschewski⁽¹⁶⁾ gives examples of the application of the Neumann-Kopp rule and compares the results with measured values. For example, he finds deviation from the measured value of Ni_2Si of +6.5 to -4.5 percent and a deviation for PbS of about 8 percent. Although no accurate calculations have been made for these materials, application of the rule indicates an increase in heat content with increasing fissium content should be expected

The heat content in the temperature range for which allotropic transformations are occurring cannot be compared from one alloy composition to another. However, in the range where all of the alloys are in a γ -phase region, good consistency in the data is apparent. A rather regular increase in heat content with increasing fissium occurs. Upon examination of the heat of fusion and heat content of the liquid material, again a regular increase is noted. Figure 9 shows this variation of heat of fusion from 0 to 8 w/o fissium alloy

The high-purity uranium data can be discussed by comparing it with the data of other workers. This is done separately for the heats of transition (in Table VIII) and for enthalpy above 0°C (in Figure 5)

Figure 9. Heat of Fusion vs. Gram Equivalent Weights

Table VIII

SOME COMPARATIVE VALUES OF TRANSITION HEATS OF URANIUM

ΔH_{fusion} : kcal/g-atom	Reported Temp ($^{\circ}\text{C}$)	Method	Source
4.7*	1133 $\pm$ 2	Vapor Pressure	Rauh and Thorn ⁽¹⁷⁾
3.7	1133 $\pm$ 2	Re-calculate vapor pressure of (17)	Stull and Sinke ⁽¹⁸⁾
3.25	1133	Estimate on (17)(18)	K. K. Kelley ⁽¹⁹⁾
3.0	1135	Estimate - theory	Brewer ⁽²⁰⁾
2.9 ± 0.3	1132.3 ± 0.5 (14)	Measure direct	This study
$\Delta H_{\alpha \rightarrow \beta}$: kcal/g-atom	Reported Temp ($^{\circ}\text{C}$)	Method	Source
0.712	662.3	Measure direct	J. M. North ⁽³⁾
0.70	662 $\pm$ 3	Measure direct	Moore and Kelley ⁽⁴⁾
0.674	668	Measure direct	Ginnings and Corruccini ⁽⁶⁾
0.665	665	Average others' data	Rossini ⁽⁵⁾
0.78 ± 0.12	667.4 ± 0.5 (14)	Measure direct	This study
$\Delta H_{\beta \rightarrow \gamma}$: kcal/g-atom	Reported Temp ($^{\circ}\text{C}$)	Method	Source
1.165	776	Average others' data	Rossini ⁽⁵⁾
1.145	772 $\pm$ 3	Measure direct	Moore and Kelley ⁽⁴⁾
1.14	777.4	Measure direct	J. M. North ⁽³⁾
1.131	774	Measure direct	Ginnings and Corruccini ⁽⁶⁾
1.1 ± 0.2	774.6 ± 0.5 (14)	Measure direct	This study

*This value may contain very large errors since it depends on a small difference of large numbers and may include systematic errors not accounted for.⁽¹⁷⁾ All other estimates except Brewer's⁽²⁰⁾ were based on this value.

Since the heats of transition can be taken only from the total enthalpy curve, the accuracy is only as good as the measured values of the enthalpy. The small differences of the enthalpy values below and above the transformations retain a large uncertainty. The percentage error possible is thus large. The mean value agrees with the measurements of other workers in the limit of our accuracy for the solid-state transformations. No attempt was made to fix the transformation temperatures here, and the most applicable reported measured values were used.⁽¹⁴⁾ There are no data reported in the literature of comparable accuracy to these for the heat of fusion, and values of estimates vary from within our accuracy limits to beyond. Calculations based on the vapor pressure measurements are prone to much greater uncertainties than these data, and most estimates were based on them. The directly measured value supersedes all the former estimates and calculated values

The enthalpy above 0°C is compared with smoothed, measured values obtained by other workers.^(3,4,6) All enthalpy data were directly measured except that of North,⁽³⁾ who calculated enthalpy from specific heat measurements in an adiabatic calorimeter. His values are lower and outside the accuracy limits of the other three sets of data. The other three sets agree within their accuracy limits. The accuracy limits in this study were determined by comparison with National Bureau of Standards measurements on sapphire, and the agreement was $\pm 2\%$. The data in this study extend beyond the temperature range of the others, and should be the most reliable at high temperatures.

VI. CONCLUSIONS

1. The total heat content from 0°C to 1200°C is 16.1 ± 0.3 , 16.3 ± 0.6 , 16.3 ± 0.6 , and 16.4 ± 0.4 kilocalories per equivalent gram atom, for the 0, 3, 5, and 8 w/o fissium alloys, respectively.

2. The heat content increases with increasing content of fissium elements, when compared on a unit weight basis.

3. The heat of fusion of high-purity uranium was found to be 2.9 ± 0.3 kcal/g-atom.

4. The heat of fusion of the alloys (heat to melt between solidus and liquidus) increases with increasing fissium content to 3.9 ± 0.4 kcal/g-atom of uranium-8 w/o fissium alloy. The heats of fusion are difficult to compare since the alloys do not melt isothermally.

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Appendix

Calculation of the Non-steady-state Heat of Transformation

The data recorded in the non-steady state determinations consist of inverse rates of heating and total times to pass through transformations. The data can be manipulated to obtain specific heats or can be used directly in comparison methods; the latter is the procedure used herein.

The heat flux through the crucible wall is determined as a function of temperature from separate measurements with the empty crucible and the crucible containing a copper standard. The unknown of like geometry is placed in the crucible, and the same measurements as before are made.

The inverse rate of heating of the stable material is obtained above and below the transformation. An interpolation of these rates gives the time that should be required to heat through a given temperature increment in the absence of a phase change. The actual elapsed time has been measured, and subtraction yields the time increase due to the phase change. Multiplication by the heat flux determined from the copper measurements gives the total quantity of heat involved.

Thus, for the uranium-3 w/o fissium alloy:

Time to heat from 21.5 to 23.9 mv	47.29 min
Average base inverse heating rate 1.02 min/0.2 mv	
Total estimated heating time $1.02 \times (2.4/0.2)$	<u>12.24 min</u>
Net time due to phase change	35.05 min

Heating rate of crucible at 22.4 mv = 41.1 cal/min
 Total heat due to phase change $41.1 \times 35.05 = 1440.55$ cal
 Weight of specimen 173.804 g
 Heat of transformation $1440.55/173.804 = 8.29 = 8.3$ cal/g.

These data were rounded to two significant figures because there was but a single run, and previous experience does not justify further significance.

CALCULATION OF THE DROP CALORIMETER ENTHALPY CHANGE

CALORIMETER DATA AND CALCULATIONS

Test Material Uranium Run No. 2 Page of

Project 279 Date 11/1/60

Drop Temp 719 °C Sample Wt. 34.2081 g Capsule Wt. - g

Starting: Time 10:12 Capill. Rdg. 4.50 cm Beaker Wt. 155.8862 gm

Ending: Time 10:52 Capill. Rdg. 4.20 Beaker Wt. 140.6331 gm

Elapsed Time 40 min Net Capill. Chg. 0.30 cm Hg. Out 15.2531

Heat Leak Correction (cm)

Time 10:05 Capill. Rdg. 4.60 cm

Time 10:10 Capill. Rdg. 4.55 cm

Net Heat Leak 0.01 cm/min

Total Capillary Correction (gm)

Mean Heat Leak 0.01 cm/min

Elapsed Time 40 min

Total Heat Leak 0.40 cm

Net Capill. Chg. -0.30 cm

Total Capill. Chg. 0.10 cm

x 0.1064 gm/cm

Total Cap. Corr. 0.0106 gm

Less Total Cap. Corr. 0.0106 gm

Heat Input, Hg. Equiv. 15.2425 gm

x 64.631 cal/gm

Net Heat Input 984.7 cal

Less: Blank Corr. - cal

Total Sample Enthalpy 984.7 cal

+ Sample Mass 34.21 gm

Unit Enthalpy 28.78 cal/gm