LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

**Adiabatic Calorimetric Enthalpy
Measurements for α , β , and γ Uranium
and the Heats of the
Transformations $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$**

by

David G. Clifton

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ADIABATIC CALORIMETRIC ENTHALPY MEASUREMENTS FOR α , β , AND γ URANIUM AND THE HEATS OF THE TRANSFORMATIONS $\alpha \rightarrow \beta$ AND $\beta \rightarrow \gamma$

by

David G. Clifton

ABSTRACT

Enthalpy of the α , β , and γ phases of high-purity depleted ^{238}U was measured, and values for the heats of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations were obtained. These measurements were made during development of an adiabatic calorimeter designed to measure heat effects on condensed-phase samples in the temperature range from about 500 to 1000°C. The calorimeter is described.

I. URANIUM ENTHALPY MEASUREMENTS

The enthalpy of a sample of high-purity depleted ^{238}U was measured during development of a high-temperature adiabatic calorimeter. Construction and operation of the calorimeter are discussed in Sec. II; the enthalpy determinations are given here.

The high-purity depleted ^{238}U was obtained from Group CMB-8 of this Laboratory, and the applicable spectrochemical analysis results are given in Table I.

Table I

SPECTROCHEMICAL ANALYSIS (ppm)

Li < 0.5	V < 25
Be < 0.5	Cr 2
B 1	Mn 3
Na < 1	Fe 70
Mg 15	Co < 5
Al 5	Ni 40
Si 50	Cu 2
P < 50	Mo < 25
Ca < 5	Cd < 1
Sn < 1	Pb < 1

Enthalpy increments were measured from about 480 to 950°C by the procedures outlined in Sec. II.

To start the experiments one must have reference points for the enthalpy values at the low-temperature end of the temperature intervals over which the measurements are made. These starting-point values for the initial temperatures (at or slightly below 500°C) were calculated from the α -uranium enthalpy equation cited by Storms.¹ Storms obtained this equation from a least-squares fit of the experimental data reported by Ginnings and Corruccini,² Moore and Kelley,³ and Savage and Seibel.⁴ The expression is

$$\alpha - \text{U}; H_T^0 - H_{298.15}^0 = 1.2840 \times 10^3 - 4.1635T + 1.3526 \times 10^{-2} T^2 - 4.1234 \times 10^{-6} T^3 - 3.3863 \times 10^{-5} T^{-1}; \text{ cal/mole, } 298 \text{ to } 940^\circ\text{K}, \pm 1.6\%, \quad (1)$$

where H_T^0 and $H_{298.15}^0$ are the enthalpy in cal/mole at T° and 298.15°C, respectively, and T is in °K.

Four low-temperature data points (initial temperatures) were thus calculated. The enthalpy values for the upper temperature points for the various experiments were then determined by adding the obtained enthalpy increments to the calculated "initial" values. To progress up the tem-

perature scale, successive temperature intervals were chosen so that their initial temperature points were within the previously determined interval. The starting value for this interval was then taken as the value obtained by graphical interpolation of the previously acquired data. The high, or end temperature, of each successive determination progressed up the temperature scale. Continuing in this manner, data were obtained for the enthalpy-temperature curves for α -U, β -U, and γ -U, including the transition points.

Table II lists the experimentally determined enthalpy values for α , β , and γ uranium in units of J/g;

they are also plotted in Fig. 1 which includes the experimental values reported by other workers. Table II also lists mean heat capacity values which are plotted in Fig. 2 as a function of temperature. This figure shows the same quantities as determined by other workers. Note that the mean heat capacity value is used primarily for intercomparison of individual works because it is merely the quantity obtained by dividing a given enthalpy by its corresponding temperature.

The following equations are linear expressions that have been fitted by least squares to the tabulated experimental data. T represents $^{\circ}\text{C}$, and the units are J/g.

Table II
EXPERIMENTAL VALUES OF ENTHALPY AND THE CORRESPONDING
MEAN HEAT CAPACITIES FOR ^{235}U

Phase	T $^{\circ}\text{C}$	$H_T^{\circ} - H_0^{\circ}\text{C}$ J/g	$(H_T^{\circ} - H_0^{\circ}\text{C})/T$ cal/mole $^{\circ}\text{C}$	Phase	T $^{\circ}\text{C}$	$H_T^{\circ} - H_0^{\circ}\text{C}$ J/g	$(H_T^{\circ} - H_0^{\circ}\text{C})/T$ cal/mole $^{\circ}\text{C}$
α	541.5	77.9	8.18	β	671.2	115.2	9.77
	550.3	77.6	8.02		676.5	115.7	9.73
	555.9	81.2	8.31		679.0	116.8	9.78
	556.2	80.0	8.18		683.7	116.8	9.72
	588.2	87.1	8.43		685.2	117.9	9.79
	605.1	90.2	8.48		685.3	118.0	9.79
	607.2	90.0	8.43		685.3	117.5	9.76
	611.6	90.2	8.39		690.9	118.4	9.75
	618.7	91.8	8.44		717.5	123.5	9.79
	626.7	94.6	8.59		730.1	125.5	9.78
	638.3	96.6	8.61		731.4	125.9	9.79
	643.4	96.9	8.57		742.5	127.9	9.80
	653.2	98.9	8.62		742.6	128.2	9.82
	658.9	100.4	8.67		750.2	129.0	9.78
	659.0	100.3	8.66		752.3	129.6	9.80
	660.2	100.3	8.64		754.2	129.7	9.78
	660.9	99.7	8.58		760.1	131.0	9.80
	663.1	100.8	8.65		767.7	132.3	9.81
	663.2	100.7	8.64		768.5	132.5	9.81
	663.5	101.7	8.72		772.9	133.2	9.81
	664.0	101.3	8.68		773.4	133.1	9.79
	664.8	101.4	8.68		773.5	133.4	9.81

Phase	T $^{\circ}\text{C}$	$H_T^{\circ} - H_0^{\circ}\text{C}$ J/g	$(H_T^{\circ} - H_0^{\circ}\text{C})/T$ cal/mole $^{\circ}\text{C}$
γ	793.2	155.9	11.2
	799.0	158.0	11.3
	799.9	158.7	11.3
	800.5	158.3	11.3
	807.5	160.3	11.3
	850.5	168.0	11.2
	866.0	165.0	11.0
	900.0	175.2	11.1
	912.5	181.0	11.2
	940.4	182.1	11.0

Fig. 1. Enthalpy of uranium vs temperature.

Fig. 2. Mean heat capacity of uranium vs temperature.

$$\alpha\text{-}^{238}\text{U}; H_T^0 - H_{O^0}^0 = -27.630 + 1.939 \times 10^{-1} T$$

(550 to 670°C range) variance of fit = 0.359. (2)

$$\beta\text{-}^{238}\text{U}; H_T^0 - H_{O^0}^0 = -4.4584 + 1.7813 \times 10^{-1} T$$

(671 to 775°C range) variance of fit = 0.0554. (3)

$$\gamma\text{-}^{238}\text{U}; H_T^0 - H_{O^0}^0 = 17.826 + 1.7553 \times 10^{-1} T$$

(775 to 940°C range) variance of fit = 1.385. (4)

Comparison of our enthalpy values with those of other workers as in Fig. 1 shows that our values are higher by about 3%. This seems reasonable when the reproducibilities of only about 3.5% obtained for the apparatus correction factor (ACF) are taken into account. Random scatter of these results about the results of other workers might be expected; however, if an error were introduced by exchanging the calibration and experimental samples it could cause a systematic error of about the size we observed.

The experimental data can be reduced in two ways for the heats of transition. First, the enthalpy curves of the various phases can be extrapolated through the phase transition temperatures and the corresponding enthalpy increment can be read directly. The second method is to follow the sample temperature, T_s , directly as a function of time and from the variations in this curve determine the time interval over which the transition occurs. This interval combined with the known rate of energy input allows calculation of the heat of transition. (Voltage and current of the sample heater are read during the transition period.)

The values of 738.5 cal/mole (std. dev. $\pm 4.2\%$) and 1200 cal/mole (std. dev. $\pm 3.9\%$), respectively, for $\Delta H_{\alpha-\beta}$ and $\Delta H_{\beta-\gamma}$ given in Tables III and IV were obtained by reducing the data in the second manner. This method allowed the closest examination of the individual transition experiments; yet, transition values obtained by the first method agree very favorably with these.

Figures 3 and 4 are representative plots of the sample temperature, T_s , vs time for the $\alpha-\beta$ and $\beta-\gamma$ transitions, respectively. Superheating seems to occur in going through the $\alpha-\beta$ transition (this phenomenon was observed consistently but in varying degrees in each run), whereas the $\beta-\gamma$ transition was always more straightforward. In both cases the indicated temperatures of transition were

Table III
HEAT OF TRANSFORMATION FOR $^{238}\text{U } \alpha \rightarrow \beta$
 $\Delta H_{\alpha \rightarrow \beta}$

Run No.	$\Delta H_{\alpha \rightarrow \beta}$ cal/mole	Previously Reported Values
38	761.9	
36	773.0	Ref. 4 786 cal/mole
12	713.0	Ref. 2 674
42	737.2	Ref. 3 680
21	731.6	716.6
48	780.7	Ref. 5 707
24	696.5	
11	713.8	
Ave. Value = 738.5		Ave. = 713 cal/mole
Std. Dev. = ± 30.7 or $\pm 4.2\%$		

Table IV
HEAT OF TRANSFORMATION FOR $^{238}\text{U } \beta \rightarrow \gamma$
 $\Delta H_{\beta \rightarrow \gamma}$

Run No.	$\Delta H_{\beta \rightarrow \gamma}$ cal/mole	Previously Reported Values
45	1259	Ref. 4 1100 cal/mole
28	1132	Ref. 2 1131
50	1219	Ref. 3 1165
27	1182	1150
53	1207	Ref. 5 1138
Ave. Value = 1200		Ave. = 1137 cal/mole
Std. Dev. = ± 47.0 or $\pm 3.9\%$		

somewhat higher than Blumenthal's⁶ values. No experiments were run to account for these phenomena in greater detail.

Our values for the heats of transition are somewhat higher than those reported by other workers; however, the precision among our determinations for the $\alpha \rightarrow \beta$ transition is such as to encompass the average values reported.

II. THE CALORIMETER

A. Design

The calorimeter used to make these measurements, which is described below, is based closely upon a design by Dench.⁷ In our calorimeter, the sample

Fig. 3. Sample temperature vs time for $\alpha \rightarrow \beta$ transformations.

Fig. 4. Sample temperature vs time for $\beta \rightarrow \gamma$ transformations.

contains a temperature-sensing thermocouple and a sample heater. The sample is surrounded by an "adiabatic" shield that is surrounded in turn by a main heater surrounded by radiation shields. A series of thermocouples is so placed as to measure any temperature gradient between the exterior of the "adiabatic" shield and the exterior of the crucible that contains the sample. The entire assembly is housed in a chamber that can be evacuated.

Figure 5 is a schematic of the calorimeter, and Fig. 6 shows the calorimeter housing.

Figure 5 shows the following. A 20-mm-high, 14-mm-i.d., 0.279-mm-thick cylindrical tungsten crucible (C) with a lid, on a tungsten pedestal (D) supported by a 3.6-mm-o.d., 1.6-mm-i.d., 6.4-cm-long hollow sintered Al_2O_3 tube (A). The bottom of this tube is held in a stainless steel support, machined to fit it. The support protrudes from its 4.125-in.-o.d., 0.125-in.-thick base plate which lies on the bottom plate of the main vacuum housing. This base plate contains four holes of about 1/2-in. i.d. so that it will not interfere with evacuation of the housing. Also supported by this base plate are the bottom exterior radiation shields (s_2) that rest upon a 2-

Fig. 6. The calorimeter housing.

in.-o.d., 1-1/4-in.-high ring (B) made from 0.005-in.-thick sheet molybdenum. There are five of these radiation shields, made of sheet tantalum as are all of the radiation shields. The bottom-most shield is 0.005 in. thick and 3-1/4 in. o.d.; the other four are 0.002 in. thick. The five exterior shields at the top of the system are similar. The shields are spaced by bent tabs punched from adjacent shields.

The main heater (H_1) is supported inside the first peripheral radiation shield which is a 7.62-cm-high, 6.83-cm.-i.d. cylinder of 0.005-in.-thick tantalum. The main heater is 0.025-in.-diam bare tantalum wire, looped back and forth between insulated supports inside this first shield. At the top and bottom ends of the shield, the heater wire is coiled and supported to heat the ends of the system. The ratios of the resistance of the end heaters to side heaters were chosen to be the same as the ratios of heat capacities of the corresponding sets of radiation shields. The ends of the tantalum heater wire are brought out through sintered Al_2O_3 insulators (E) which penetrate all five of the side radiation shields. These lead wires are then connected to heavy, 0.100-in.-o.d. copper leads through the vacuum housing with glass-to-metal seals

Fig. 5. Schematic of the calorimeter.

sealed into small, 1-1/4-in.-o.d., 1/4-in.-thick brass disks that carry O-ring seals. These disks are bolted onto inlet ports in the housing.

The insulated supports for the main heater are short 5-mm lengths of two-hole sintered Al_2O_3 insulators. The heater wire is strung through one of the two holes, and a small loop of 0.015-in. tantalum wire is looped through the second hole. The loop is held by bending part of a small tab of 0.003-in.-thick sheet tantalum around it. The tab is then spot-welded to the inside of the tantalum cylinder which acts both as the support system and first cylindrical radiation shield. The four outer radiation shields are made of 0.002-in.-thick tantalum. The entire main heater assembly including the outer radiation shields rests on the bottom radiation shields.

The top set of radiation shields, which rest on the cylindrical side shields, contain two holes to permit passage of the sample heater (H_2) and the sample thermocouple (TC_1), which are kept from falling through the shields by a small wire ring wound around each. The conduit material for H_2 and TC_1 is sintered Al_2O_3 , with small notches filed into it so that the retaining wire ring will not slip. The same technique is used to support other thermocouples which will be discussed below.

The solid sample, (S), has two reentrant holes, aligned with similar sized holes in the crucible lid, to receive the sample heater (H_2) and the sample thermocouple (TC_1).

The sample heater is housed in a 1.6-mm-i.d., 3-mm-o.d., 6-cm-long Al_2O_3 sheath, closed at the bottom. The heater consists of two 0.015-in.-diam tantalum wire power leads connected to a 1-mm-o.d. coil of 0.003-in.-diam tungsten wire. The coil is about 1 cm long and has a resistance of about 3.3 Ω . The coil is connected to the tantalum leads by threading it through 0.006-in.-i.d. holes drilled transversely into the 0.015-in.-diam tantalum lead wires. The threaded ends of the tungsten coil are then bent back along the tantalum lead wire and tied into place with a 0.003-in.-diam molybdenum wire to make good electrical contact. Two potential leads of 0.003-in.-diam tantalum wire are connected to the power leads in the same manner as the tungsten coil.

Their points of attachment are located so that when the heater is in place in the sample one terminal is at the top of the crucible and the other is at the edge of the "adiabatic" shield (s_1). This procedure assigns one half of any energy generated in the power leads to the sample and the other half to lead leakage, the standard practice in making energy measurements in calorimetry. Electrical shorting between the power and potential leads is eliminated by using small, single-bore sintered Al_2O_3 insulators. Each potential lead is insulated with 0.5-mm-o.d., 0.2-mm-i.d. Al_2O_3 . One of the 0.015-in. tantalum power leads is insulated with an 0.8-mm-o.d., 0.4-mm-i.d. piece of Al_2O_3 . The heater and these leads all slide into the closed-end 3-mm-o.d. Al_2O_3 sheath. The potential leads are then taken to terminals that pass through the main vacuum housing through glass-to-metal seals.

The sample thermocouple (TC_1) and all the other thermocouples are made of 0.005-in.-diam Pt and Pt-10% Rh. The wires are threaded through 1.55-mm-o.d. sintered Al_2O_3 insulators with two 0.4-mm-i.d. holes. All of the insulating materials are from DeGussa, Inc., and are described as AL 23, a dense, 99.5% pure Al_2O_3 that has been sintered to 1800°C. The sensing beads of all thermocouples are much smaller than the outside diameter of their insulators, and are always installed so that they do not touch any surface or short to ground.

The set of shields (s_1) immediately surrounding the sample crucible are the "adiabatic" shields. The bottom one is a 34.9-mm-o.d., 0.005-in.-thick tantalum disk; the top one is the same except for the two holes for the sample thermocouple and heater. The bottom shield slides onto the pedestal support rod (A) and is held in place by the wire ring and notch arrangement described previously. The top shield rests on the cylindrical side shield, made of 0.005-in.-thick tantalum, 27 mm high and 25.4 mm i.d. This cylinder has spot-welded to it three small pods or boxes (F) open at the bottom. The pods are 0.002-in.-thick tantalum strips spot-welded together and bent to shape and then spot-welded to the shield. Three more of these pods (F) are tied to the crucible (C) and held in good thermal contact with it by being wired securely in place with 0.015-in. tantalum wire.

The two sets of pods are radially aligned at 120° intervals. The pods act as housings for the six ΔT -sensing thermocouples (TC_2) through (TC_7) which sense any temperature gradient, ΔT , between the exteriors of the crucible and the adiabatic shield. The thermocouples are therefore never exposed directly by line of sight to the external heater windings.

The six ΔT -sensing thermocouples are insulated with 1.6-mm-o.d., 0.4-mm-i.d., two-holed sintered Al_2O_3 and brought up from the bottom of the system through the bottom outer radiation shields (s_2) and the adiabatic shield. They are held in place by sheet tantalum stirrups (J) spot-welded to the bottom shield, and by the usual wire-ring and notch arrangement. The leads for each of these six thermocouples and the sample thermocouple are insulated with Al_2O_3 out to where they go through the main vacuum housing. The seals through the housing are a commercial seal consisting of small hollow metal tubes about 0.040 in. i.d. set into glass that insulates the individual tubes from a mounting flange. The flanges are soldered into holes in 1-1/4-in.-o.d., 1/4-in.-thick brass disks that have O-ring seals and are bolted onto inlet ports. It was necessary to insulate the Pt and Pt-10% Rh leads from the metal tubes of these seals with Al_2O_3 of small outside diameter and to make the final vacuum seal for the lead-throughs with epoxy resin. Without this precaution there were thermally sensitive areas at these lead-through points.

The other item shown in Fig. 5, is a 4-7/8-in.-high, 3/32-in.-thick, 4-3/16-in.-o.d. stainless steel cylinder (G). This unit is set down around the calorimeter assembly and rests on the bottom of the main housing and helps protect the outer brass walls of the main housing from excessive heat.

Figure 6 is a schematic of the main vacuum housing system for the calorimeter. The housing is a brass cylinder (A), 3-1/4 in. high and 3-1/8 in. o.d., with 1/8-in.-thick walls. A 1/4-in.-thick brass ring (B) has been silver soldered to each end of this cylinder. The periphery of each of these brass rings is octagonal, measuring 6 in. from flat to flat. Sealed to each of these rings by O-ring seals are octagonal brass rings (C), 1-1/4 in.

high and 7/8 in. thick. In each of the flats of these rings are 1/2-in.-diam circular ports used for lead-in access to the calorimeter. The lead-ins are brought through 1/4-in.-thick, 1-1/4-in.-o.d. brass disks (E) which have O-ring seals and are bolted into place. The various lead-in systems such as glass-to-metal seals, Fairchild Recording Equipment Corporation Conax seals, or valves, are soldered into the brass disks. (See items (F) and (G) in Fig. 6.) Both the top and bottom octagonal port rings have two O-ring grooves, one to seal to the main vacuum housing (A) and one to seal to the top and bottom plates (H) and (J), respectively. The lid (H) is held by bolts (K), and the whole assembly is bolted to the base plate (J). This base plate is soldered to a 1-1/2-in.-i.d. copper tube (L) which goes to a Veeco Instruments, Inc., high-vacuum valve (M) and then to a vacuum system. Cooling coils (N) of 3/8-in.-o.d. soft copper tubing have been soldered to plates that are bolted to the lid and bottom plates of the housing. Cold water is circulated through these coils. The cooling coils for the main body of the housing are fixed to a hinged clam-shell arrangement of 1/8-in.-thick brass which is held snugly against the main housing. The entire cooling coil system can be removed from the housing. The connection to the vacuum pumping system below the Veeco valve is made through a flange with an O-ring seal. This design of removable cooling coils and an isolation valve permits the entire calorimeter housing, exclusive of the vacuum system, to be removed and transported within a complex of dryboxes. This feature was deemed useful for measuring plutonium compounds.

The vacuum pumping system consists of an octagonal collar, with inlet ports similar to those described above, to which the housing is mated. These ports are used to mount vacuum gauges. Mounted in the collar are two Veeco Type DV-1M thermocouple vacuum gauges and one Veeco RG-75 ionization gauge which are read with a Veeco RG-31X control unit. A Consolidated Vacuum Corporation (CVC) high-vacuum sliding valve, type VCS-41B-WF, isolates the inlet collar system from a CVC water-cooled chevron baffle that is set on the top of a 4-in. CVC Model PAS-41C oil diffusion pump backed by a Welch Scientific Company Duo-Seal, Model 1397 forepump.

The entire system can be evacuated to about 5×10^{-6} mm Hg and kept at this pressure while a sample is heated to 1200°C .

B. Instrumentation

During calorimeter operation it is necessary to measure the sample temperature determined by thermocouple TC_1 as a function of time. The signal corresponding to the temperature gradient, ΔT , obtained from the six thermocouples (TC_2) through (TC_7) is also monitored. All of these thermocouples have been wired so that their individual legs are brought out of the housing. The seven pairs of leads are connected through extension leads to a terminal strip located in a box that has a uniform temperature. At this terminal strip, connections are made to the leads of a 10-position Leeds & Northrup Company No. 8248 thermocouple rotary selector switch. A reference junction thermocouple of Pt-Pt 10% Rh that is kept in an ice- H_2O system at 0°C is connected in series (in the uniform temperature zone) to the output leads of the rotary selector switch. This permits reading the emf's from the individual thermocouples. Also at the terminal strip, appropriate connections are made, through a series of switches, from the individual thermocouples comprising the three pairs of ΔT -sensing thermocouples so that six couples can be ganged in series, with the resulting emf being switched to a potentiometer. The wiring diagram and switching arrangement to facilitate these readings are shown in Fig. 7.

The emf readings of these thermocouple systems can be observed with either of two instrument arrangements. One arrangement consists of the usual null-balancing system composed of a Leeds & Northrup 7555 K-5 potentiometer, a Leeds & Northrup mirror and light galvanometer with a sensitivity of $0.44 \mu\text{V/mm}$, a Leeds & Northrup guarded dc constant-voltage power supply No. 9879, and a Muirhead Instruments, Inc., standard cell, which was calibrated by the P-Division standards group of this Laboratory. The second instrument was a digital voltmeter (CVM), a Doric Scientific Corporation Model DS-100 integrating microvoltmeter with scale ranges of 10 and 100 mV and 1, 10, 100, and 750V. Generally this latter instrument allows readings to $\pm 1 \mu\text{V}$ and permits

Fig. 7. Wiring diagram for ΔT sensors.

fast readings when the sample temperature is changing rapidly.

In the course of an experiment, the sample temperature is usually read with the DVM, and the ΔT -sensing couples are ganged in series, with the resulting ΔT signal being read with the K-5 system. Because this ΔT -sensing signal is used to "balance" the adiabatic feature of the calorimeter, observations of movements in the mirror and light galvanometer are used to follow any variations in ΔT .

The switching system shown in Fig. 7 is also designed to allow the ΔT signal to be used in an automatic control circuit to regulate the power supplied to the main heater; however, for the work presented here this automatic feature was not used.

Power for the main heater, H_1 , of the calorimeter is supplied by a programmable, constant-voltage, Harrison Labs, Inc., Model 627 4A dc power supply with 0- to 60-V, 0- to 15-A output. The output can be controlled by a 10-turn precision Beckman Instruments, Inc., Heipot, Model A, with $200\text{-}\Omega$ resistance and 0.05% linearity. Although this supply is rigged for automatic control

through the ΔT -sensing signal, this feature was not used because it has not been refined enough for practical use.

One of the requisites of experiments in the calorimeter is measurement of the total amount of energy added to the sample through the sample heater, H_2 . This is done by measuring the voltage drop across the heater potential leads, the current through the heater, and the heating time interval. The power to heater H_2 is supplied by a programmable, constant-voltage Hewlett-Packard Company Model 6113A dc power supply with 0- to 10-V, 0.2-A output. The potential drop across the heater is read by the DVM described above. This meter is connected through a selector switch that permits it to be switched to several stations for different readings: the voltage drop across the sample heater, E_h ; the voltage drop across a standard 1- Ω resistor (Gary Instrument Co. standard resistor Model E-1243 which is 1 absolute ohm) in series with the heater, I_h ; the voltage across a storage condenser in an integrating circuit, $I_h dt$; the voltage output of the sample thermocouple, TC_1 ; and any voltage impressed across an extra set of terminals. The lead from the heater power supply to the heater contains a switch so wired that when it is closed to apply a pre-programmed voltage to the heater it simultaneously closes a power line to a timer with a digital display. The timer is a Burroughs Corporation Model BSB-59-4 which can be read to 0.001 min. With this arrangement it is possible to read the constant voltage across the heater, the current through the heater, and the time interval of the energy addition.

Another feature of the sample heater circuitry is the use of an operational amplifier as an integrating circuit so that the actual value of the integral of current and time can be read directly. This eliminates having to take into account the variation of the current as a function of time. The value of this integral can be displayed on the DVM when the selector switch is properly set. Normally this reading is made at the very end of the heating period, and then a series of further readings are taken as a function of time to account for any slow leaks in the storage capacitor circuitry. This integrator system has been precalibrated and found reliable to within about 0.07%.

C. Operating Procedures and Calibration

The operation of an adiabatic calorimeter is based on having a sample at some temperature surrounded by an adiabatic shield kept at the same temperature so that there is no heat exchange between the sample and its surroundings. If known amounts of energy can be added to or taken from the sample, and its temperature can be followed while the adiabatic shield temperature is manipulated simultaneously to follow that of the sample, thermal effects can be measured quantitatively. In practice, such an ideal system cannot be attained because there must be sample support structures, a sample heater, heater leads, temperature measuring devices and leads, and other accessories that not only contribute to the thermal effects because of their heat capacities, but also provide paths for heat leaks and cause thermal asymmetries in the apparatus. Because of these practical difficulties, each calorimeter system has individual characteristics; therefore, development of any such instrument requires investigation of its particular behavior under varying experimental conditions.

Because of the uniqueness of each calorimeter and the necessity for experimental development before actual measurement of an unknown sample, some of the experimental data obtained for the calorimeter described here are presented.

The samples of interest for this calorimeter were solid cylinders with two reentry holes in the top. To provide some samples with known thermal properties, several samples of single-crystal Al_2O_3 or synthetic sapphire were obtained from the Electronics Division of the Union Carbide Corporation. Two of these samples that were used frequently were sample No. 1, a 14-mm-high, 12-mm-o.d. cylinder, weighing 5.9020 g, and sample No. 3, an 18-mm-high, 12-mm-o.d. cylinder, weighing 7.5635 g. At the start of the calorimeter development, many observations were made upon sample No. 3 and repeated with sample No. 1. This was done primarily to observe the effects upon some of the measured parameters when one sample was removed and another sample was introduced into the system. It is necessary to remove the top radiation shields, sample heater, sample thermocouple,

crucible lid, and crucible to replace a sample. This process disturbs the relative positions of some of the radiation shields and can cause slight displacements of the main heater assembly; consequently, variations were found in some of the measured parameters. Rather than detail all of these measurements, we will discuss the basic results of similar measurements made just before acquisition of the uranium data.

In some of the early experiments, the adiabatic shield system was a three-shield-thick arrangement similar to the outer radiation shields. This was found to impose an intolerably long response time upon the ΔT -sensing thermocouples because of thermal lags between the outer and inner thermocouples. Therefore, a single 0.005-in.-thick tantalum adiabatic shield was adopted. Another modification resulting from early experiments was the addition of the shielding pods on the adiabatic shield and crucibles; originally, these thermocouples were bare and did not reflect the exterior shield temperature nor crucible temperature closely.

The earlier experiments were repeated with a known sample in place after the above adjustments had been made. These experiments were done with the No. 3 sample of Al_2O_3 , and some of the data are now given.

After sample No. 3 was introduced and the calorimeter was evacuated, the main heater power supply (PS No. 1) was set to a given output by turning the 10-turn Helipot to a given dial reading and the system was allowed to equilibrate. Equilibration was determined by reading the sample temperature, T_s , as a function of time until T_s became steady. After equilibration, the sample temperature, T_s , the output voltage and current of PS No. 1, the ΔT signal from the six sensing thermocouples switched into the series position, and the individual temperatures, T_i , of each of these thermocouples were read.

An obvious feature of this series of experiments is the extreme slowness with which the calorimeter equilibrated at 500°C or below. Because the primary mode of heat transfer in the evacuated system is radiative, this slowness is expected at the lower temperatures at which the rate of radiative heat transfer is low. Because

of this slow equilibration, the ΔT -sensing couples respond slowly so that attempts to control the ΔT gradient by manipulation of PS No. 1 cause bad overshoots. Conversely, at the higher temperatures equilibration is rapid. The low-temperature range of the calorimeter could probably be extended by the introduction of a gas such as helium, but this was not done.

Figure 8 is a plot of the steady-state sample temperature, T_s , vs the dial settings of the Helipot control of PS No. 1. Note that these data points were not all determined in ascending order. There seemed to be no dependency on the order of data acquisition, and each point was reasonably reproducible.

Figure 9 shows the output power of PS No. 1 vs the steady-state sample temperature. The scatter in these data is understandable because the output meters of PS No. 1 cannot be read precisely. Our main interest in these data is that extrapolation of the curve indicates that the calorimeter probably would require only 1000 W or less to attain 1400°C.

Fig. 8. Sample temperature vs dial setting of power supply.

Fig. 9. Main heater power output vs sample temperature.

Figure 10 is a plot of the ΔT signal as emf vs the steady-state sample temperature. This ΔT signal corresponds to the ganging of the six thermocouples in series, and, therefore, if it is divided by 3 it approximately represents the emf generated between two thermocouples, one on the exterior of the shield and its radially aligned mate on the crucible. Conversion of these average emf values per pair of thermocouples to temperature by dividing them by the appropriate emf/ $^{\circ}\text{C}$ for the Pt-Pt-10% Rh thermocouples shows that the ΔT values range from about 3.0 to about 4.2 $^{\circ}\text{C}$ between T_g values of 500 and 950 $^{\circ}\text{C}$, respectively. These ΔT values are verified by analysis of the individual thermocouple readings. Furthermore, the slight upward trend in the emf vs T_g graph is partly due to the increase in emf/ $^{\circ}\text{C}$ found for the Pt-Pt-10% Rh thermocouple in going from 500 to 950 $^{\circ}\text{C}$.

These data also show that the temperature gradient is such that the exterior of the shield has a higher T than the exterior of the crucible. These sensing thermocouples do not read the actual temperatures of the exterior of the shield or crucible because of lack of direct contact and lead losses, but they do reflect a steady-state response to these temperatures. Also, their locations preclude these thermocouples from measuring temperatures near the top or bottom of the crucible where the supports and leads are located. Despite these limitations, the direction of the temperature gradient is significant; i.e., the exterior of the shield is hotter than the crucible, which indicates that the sample tends to reach a steady state rather than a uniform temperature, when T_g no longer changes with time. Probably, energy flows into the

sample area from the main heater and from the sample area through the support system, heater leads, thermocouple leads, and insulator supports. Because this indicates possible temperature gradients in the sample, some indication of the reliability of the sample temperature, T_g , readings is of interest. Such data are available from the experiments on the uranium sample reported above. The temperatures of the uranium sample when it goes through the α - β and β - γ transitions can be compared with the temperatures accepted for these transitions by Blumenthal.⁶ These comparisons indicate that T_g read at these two points, 667 and 775 $^{\circ}\text{C}$, are about 3.5 to 4.5 $^{\circ}$ high; however, the sample heater was on and its proximity could account for part of this discrepancy. In contrast, when temperatures were read during a γ - β transition (sample heater off), the T_g read only 1 $^{\circ}$ low. The sample temperature readings are assumed good to about $\pm 5^{\circ}\text{C}$.

The integrating circuitry used to measure the energy added to the sample was calibrated by a series of measurements. The output of the sample heater power supply (PS No. 2) was connected to a load of a standard resistor and a standard resistance voltage divider. Voltage drop measurements made with the K-5 potentiometer were then converted into current, and used in conjunction with a time measurement to obtain the current-time product. As the current was constant for these experiments, this product corresponds to the current-time integral. While these measurements were being made, the integrating circuit was also running, so the value for the current-time integral from the integrator was available. The tests covered the current range from 0.05 to 0.75 A, and the agreement between the two integral values was within 0.07% in all cases. This is considered adequate for determination of the energy added. The voltage supply, PS No. 2, is a regulated constant dc voltage power supply and is constant to better than 0.1%, so the total energy determination is considered known to about 0.1%.

To determine enthalpy increments of a sample, the following procedures are followed. The PS No. 1 output value is set through the Helipot dial to give the desired approximate starting temperature, T_1 . This is estimated from Fig. 8. The calorimeter is allowed to come to a

Fig. 10. Temperature gradient ΔT , vs sample temperature.

steady state. Next, the ΔT signal from the sensing thermocouples (ganged in series) is balanced and read with the K-5 potentiometer and the mirror and light galvanometer. As can be seen from Fig. 10, this ΔT signal is practically the same over the entire temperature range from 500 to 950°C. Therefore, if one maintains this ΔT value while adding energy to the sample from the sample heater by adjusting the power to the main heater, the heat leaks to or from the sample are assumed to be minimal. Changes in the ΔT signal are observed as deflections of the mirror and light galvanometer from the null point.

To make the enthalpy increment measurement, after the system is at steady state, T_1 , and with the ΔT signal nulled out, a preprogrammed voltage is set into the sample heater power supply, PS No. 2, and it and the timer are turned on simultaneously. The voltage across the sample heater, the sample temperature, and the time are now read. The sample temperature readings are made at half-minute intervals, and as T_s rises the ΔT signal becomes unbalanced and the galvanometer moves from the null point. The 10-turn Helipot on PS No. 1 is then manipulated to keep the ΔT signal at the null point. The balancing and recording of T_s and time are continued until the desired amount of energy has been added, then PS No. 2 is turned off. The integral value of the integrator and time are read immediately, ΔT signal balancing is no longer required, and readings of T_s and time are continued for about 15 min. During the postheating period, several readings are made of the integrator as a function of time, because these readings show a slight leak from the integrator storage capacitor and consequently are used to apply a slight correction to the originally recorded value. A plot of the sample temperature, T_s , vs time is used to obtain a final sample temperature, T_2 .

The acquired data give an input energy, ΔF , needed to go from T_1 to T_2 . This amount of energy includes not only that needed for the sample but also any losses and that energy needed because of the heat capacities of the support system, heater, thermocouple, etc. To correct for these terms, one must have an apparatus correction factor or energy-equivalent type of correction which can be obtained from the following series of measure-

ments. Enthalpy determinations similar to the above were made upon a known weight of Al_2O_3 , sample No. 3. Taking the known enthalpy values of Al_2O_3 as given by Furukawa et al.⁸ up to 1200°K and the values given by Kantor et al.⁹ above 1200°K, the energy required to take the Al_2O_3 sample through a given temperature interval is considered known. Subtraction of this value from a measured total energy input for the given ΔT interval leaves the energy contributed to the apparatus for this temperature interval. Division of this energy by the apparatus by the corresponding ΔT gives the apparatus correction factor, ACF.

Figure 11 shows this apparatus correction factor plotted against the sample temperature. These data were taken on the Al_2O_3 sample No. 3 just before making the experimental runs on uranium. The plot shows the ACF values for various temperature intervals.

Previous to the determinations shown in Fig. 11, two other such series had been made on Al_2O_3 samples No. 1 and No. 3. The reproducibility of these ACF values, which involved the replacement of one sample with another and the consequent disturbances to the apparatus, was about 3.3%.

From the data plotted in Fig. 11, the ACF value obtained and subsequently used for the uranium measurements is 4.37 J/°C with a standard deviation of $\pm 3.1\%$ among 20 determinations. In deducing this value from the data, two experimental values at the low-temperature end of the experiments were rejected. This was justified because at the lower temperatures the sluggish response of the ΔT sensors increases the possibility of introducing errors and decreases reproducibility.

Fig. 11. Apparatus calibration factor, ACF, vs sample temperature.

To obtain data upon an unknown sample, such as the data for uranium reported above, one proceeds as follows. Remove the calibration sample, in this case, Al_2O_3 sample No. 3, and replace it with the uranium sample. Determine the total added energy, ΔE , corresponding to a given temperature interval, T_1 to T_2 . From this total added energy, subtract the value of the product of the apparatus correction factor, ACF, and the temperature interval, T_1 to T_2 ; the result is the amount of energy needed to take the unknown through the temperature interval, T_1 to T_2 .

There seemed to be a limitation on the high-temperature end of the calorimeter at about 950 to 1000°C. This difficulty showed up as erratic behavior in the temperature gradient, ΔT , signal and precluded using this signal to balance out the system. Further development of the calorimeter would be necessary to establish the cause of the poor behavior near 1000°C. Conceivably, the disturbances could be due to thermionic emission of the thermocouples or to some stray electrical pickup, but the cause was not experimentally determined.

III. REFERENCES

1. E. K. Storms, "The Refractory Carbides," Academic Press, New York, 1967, p. 191.
2. D. C. Ginnings and R. J. Corruccini, J. Res. Natl. Bur. Stds. **39**, 309 (1947).
3. G. E. Moore and K. K. Kelley, J. Am. Chem. Soc. **69**, 2105 (1947).
4. H. Savage and R. D. Seibel, Argonne National Laboratory Report ANL-6702 (1963).
5. J. M. North, Atomic Energy Research Establishment Report A.E.R.E. M/R 1016 (1952).
6. B. Blumenthal, J. Nucl. Mater. **2**, 23 (1959).
7. W. A. Dench, Trans. Faraday Soc. **59**, 1275 (1963).
8. G. T. Furukawa, T. B. Douglas, R. E. McCoskey, and D. C. Ginnings, J. Res. Natl. Bur. Stds. **57**, 67 (1956).
9. P. B. Kantor, L. S. Lazaryeva, V. V. Kandyba, and Y. M. Formickov, Ukr. Fiz. Zh. **7** (2), 205-211 (1962).