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THE TRANSFORMATION TEMPERATURES OF HIGH-PURITY URANIUM

by

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and L. T. Lloyd

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

THE TRANSFORMATION TEMPERATURES OF HIGH-PURITY URANIUM

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ABSTRACT

The transformation temperatures of high-purity uranium were determined by thermal analysis and dilatometry. Two thermal analysis methods were used: one in which the rates of heating and cooling were controlled by a differential thermocouple and another in which repeated thermal analyses were made at independently controlled rates. The solid-state transformation temperatures and the logarithm of the heating or cooling rates at relatively low rates are related linearly. The extrapolated functions intersect at a point where the disturbing effects of hysteresis, superheating and undercooling disappear, i.e., at the equilibrium temperature. The mean transformation temperatures are 667°C for $\alpha \rightleftharpoons \beta$ and 775°C for $\beta \rightleftharpoons \gamma$. The mean temperature for melting and freezing is 1132°C.

I. INTRODUCTION

Measurements of the solid-state transformation temperatures of uranium were made as early as 1942 and of its melting point in 1930. The early data were reviewed by Katz and Rabinowitch.[1] Few of these measurements have any significance today since they were made on rather impure metal under conditions where the formation of large quantities of oxide and nitride was inevitable. Nevertheless, Chipman[2] reported in 1946, in summarizing the work of the Metallurgical Laboratory, an $\alpha \rightleftharpoons \beta$ transformation temperature of 665°C, a $\beta \rightleftharpoons \gamma$ transformation temperature of 775°C and a melting point of 1130°C; these data approach present measurements.

In making heat content measurements, Moore and Kelley[3] found two sharp transitions at 662 ± 3°C and 772 ± 3°C with no evidence of hysteresis. Resistivity measurements by Dahl and Van Dusen,[4] however, revealed a large hysteresis for the solid-state transformations. Their data were:

$\alpha \rightarrow \beta$ = 667°C $\beta \rightarrow \gamma$ = 772°C

$\beta \rightarrow \alpha$ = 645°C $\gamma \rightarrow \beta$ = 764°C

The data by Dahl and Van Dusen were evaluated by Ginnings and Corrucini[5] for the purpose of calculating heats of transition. They used 668°C and 774°C, for the respective transformation temperatures, probably the highest values obtained by Dahl and Van Dusen. Similar results were obtained by some of the investigators of binary phase diagrams; their data are shown in Table I.

TABLE I

Solid-state Transformation Points of Uranium from Binary Phase Diagrams

Authors	Year	Transformation Temperatures (°C)				Rate of Heating or Cooling (°C/min)
		$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$	$\beta \rightarrow \gamma$	$\gamma \rightarrow \beta$	
Gordon and Kaufmann[6]	1950	655*		765*		5 to 10 and 1
Grogan[7]	1950	675	660	780	770	
Buzzard, Liss and Fickle[8]	1953	-	657	-	768	2
Buzzard, Fickle and Park[9,10]	1954	-	653	-	762	2
Knapton[11]	1954	667	637	773	757	1**
Chiotti, Tracy and Wilhelm[12]	1956	666 ± 2	655 ± 2	771 ± 2	766 ± 2	5
Catterall, Grogan and Pleasance[13]	1956	665 ± 3		772 ± 3		10

*Transformations took place over a range of temperature of 5°C at a rate of 1 °C/min

**By dilatometry; all others by thermal analysis.

While these results appeared to be fairly consistent, they were, nevertheless, looked upon with suspicion, partly because of the impurity content of the metal and partly because of the large hysteresis effects, even at low rates of heating and cooling. The very large effect of the cooling rate on the transformation temperatures was shown by Duwez,[14] who, using a rate of 8000°C/sec, obtained supercooling of the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations by about 200°C and 300°C, respectively.

Only one reliable datum exists for the $\gamma \rightleftharpoons L$ phase change. Dahl and Cleaves[15] determined the freezing point ($L \rightarrow \gamma$ only) by taking a sequence of cooling curves at a rate of 1°C/min. Successive determinations resulted in an increase of the freezing point from 1125°C to 1133°C. Simultaneously, a reduction of the carbon content was observed in the melt; the highest freezing point was associated with a carbon content of 6 ppm. Most of the other observers report data below 1133°C without specifying the carbon content or other analytical data.

With the advent of high-purity uranium and the development of precise analytical methods for impurity determinations it became possible, and indeed desirable, to redetermine the transformation

temperatures. This also became necessary as part of a uranium-carbon alloy study by Blumenthal,[16] where only small temperature effects were expected.

The work described in this report consists of three parts:

1. A determination of the three transformation temperatures at rates controlled by the differential thermocouple arrangement first proposed by Smith.[17] (J. E. Baumrucker)
2. A precision determination of the three transformation temperatures by repeated thermal analyses at independently controlled rates. (B. Blumenthal)
3. A determination of the solid-state transformations by a dilatometric method. (L. T. Lloyd)

II. MATERIALS

The materials used in all three investigations were remelted high-purity electrolytic uranium; the pertinent analytical data are given in Tables II, III, and IV. Some dilatometric measurements were made on remelted biscuit metal and others on reactor-grade uranium. The analytical data for the less pure materials are given in Table V.

TABLE II

Composition of High-purity Uranium used by Baumrucker

Specimen No.	Sample Location	Chemical Analysis (ppm)*		Spectrochemical Analysis** (ppm)						
		C	N	Al	Cr	Cu	Fe	Mg	Mn	Si
B-327	Bottom	-	-	5	3	1	8	0.5	1	<10
	Top	19-45	7-13	5	3	4	8	0.5	1	<10
	Core	31-60	10-20	5	3	2	8	0.5	1	<10
B-369	Bottom	15	<10	<5	<1	1	2	0.5	1	15
	Top	17	14	<5	<1	2	2	0.5	1	15
	Core	-	-	<0	<1	2	10	2	1	10
B-370	Top	17	-	5	<1	1	3	0.5	1	10
	Core	22	-	5	<1	2	2	0.5	1	10
B-417	Bottom	35-55	<10	5	1	1	3	0.5	0.5	<10
	Top	48-55	28-32	5	1	2	10	0.5	2	10
	Core	-	-	5	1	1	3	0.5	0.5	10
B-427	Bottom	-	-	10	1	2	5	0.5	0.5	10
	Top	25	-	10	1	1	2	0.5	0.5	10
	Core	-	-	10	1	1	10	0.5	0.5	10

*All analyses are given in parts per million by weight.

**All other elements below limits of spectrochemical detection.

TABLE III

Composition of High-purity Uranium Used by Blumenthal

Spec. No.	Chemical Analysis (ppm)*				Spectrochemical Analysis** (ppm)							Remarks
	H	C	N	O	Al	Cr	Cu	Fe	Mg	Mn	Si	
B-721	-	26-35	<10	-	7	<1	1	2	1	<1	10	Before thermal analysis
	-	28-37	<10-19	1	7	<1	1	2	1	<1	20	After thermal analysis
B-724	-	26-35	<10	-	7	<1	1	2	1	<1	10	Before thermal analysis
	-	22-25	<10	1	7	<1	1	2	2	<1	10-15	After thermal analysis
B-726	-	34-40	<10	6.6	5	<1	1	2	1	<1	20	Before thermal analysis
	-	40-50	<10	2	7	<1	1	2	1	<1	10	After thermal analysis
B-728T	.21	5	<10	22-25	5	1	1	7	<1	<1	15	Used in solid state only
B-734	-	7-10	12	25-26	5	<1	1	2	1	<1	10	Used in solid state only

*All analyses are given in parts per million by weight.

**All other elements below limits of spectrochemical detection.

TABLE IV

Composition of High-purity Uranium Used by Lloyd

Specimen No.	Chemical Analysis (ppm)*			Spectrochemical Analysis** (ppm)							
	C	N	O	Al	B	Cr	Cu	Fe	Mg	Mn	Si
B-183	15,23	9,22	n.d.	<10	0.2	<1	3	3	2	<.5	3
B-272	8,11	18	n.d.	5	<1	<1	1	7	<.5	.5	5

*All analyses are in parts per million by weight.

**All other elements below limits of spectrochemical detection

TABLE V

Composition of Impure Uranium Used by Lloyd

Spec. No.	Material	Chemical Analysis (ppm)*			Spectrochemical Analysis** (ppm)								
		C	N	O	Al	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Si
B4-1	Reactor-grade Uranium	436	29	3 to 12	10	3	3	50	1	5	10	30	30
B-246	Remelted Biscuit Uranium	20	12	n.d.	10	2	5	30	10	5	10	2	20

*All analyses are in parts per million by weight.

**All other elements below limits of spectrochemical detection.

III. EXPERIMENTAL APPARATUS

The apparatus used by Baumrucker is shown in Figure 1. Its high-vacuum resistance furnace consisted of a water-cooled stainless steel shell into which were placed a tubular molybdenum wire-wound ceramic heater and a series of tantalum and molybdenum radiation shields. The specimen, in the form of a tapering cylinder which conformed to the internal contour of the urania crucible, was in the center of the furnace. It had a diameter of 7/8 in. at the top and was about 2 in. long with a 1/4-in. diameter center hole lengthwise to receive the thermocouple protection tube.

The vacuum system consisted of the following components, starting at the furnace: a pot-type liquid nitrogen cold trap, a water-cooled baffle, a 6-in. fractionating oil diffusion pump (MCF 700 by Consolidated Engineering Corp.), a 4-in. oil diffusion booster pump (MB 100 by Consolidated), and a two-stage mechanical forepump of 375-liter/min free air capacity (No. 1397 by Welch). Vacua attained were approximately 10^{-5} mm Hg at melting and 10^{-6} to 10^{-7} mm Hg at room temperature.

Two Pt/Pt-10% Rh thermocouples were used to measure and control the temperature of the furnace, to control the rate of heating and cooling, and to measure the arrest temperatures. The central thermocouple continuously recorded the specimen temperature by means of a 3-millivolt span, multirange Leeds and Northrup Speedomax recorder. Heating and cooling rates were controlled by a dual-range Leeds and Northrup differential controller-recorder using a thermocouple contacting the outside of the crucible (see Figure 1) in conjunction with the central recording thermocouple. The controller was connected to a contactor for an on-off control of the furnace power.

The transformation temperatures were measured during the arrests, of many minutes duration, by means of a Rubicon precision potentiometer, using the central thermocouple disconnected from its recorder. The cold junctions were held at 0°C in an ice bath.

The thermocouples were calibrated against a couple obtained from the National Bureau of Standards. The readings of the measuring couple were converted to degrees centigrade by means of the NBS reference tables (Circular No. 561); appropriate corrections were applied.

The experimental apparatus used by Blumenthal was a modified version of the high-vacuum Globar resistance furnace described previously.[18] Its vacuum system was left unchanged. The heating system was rebuilt to permit repeated thermal analyses at a predetermined, yet variable, rate unaffected by load oscillations caused by the common on-off

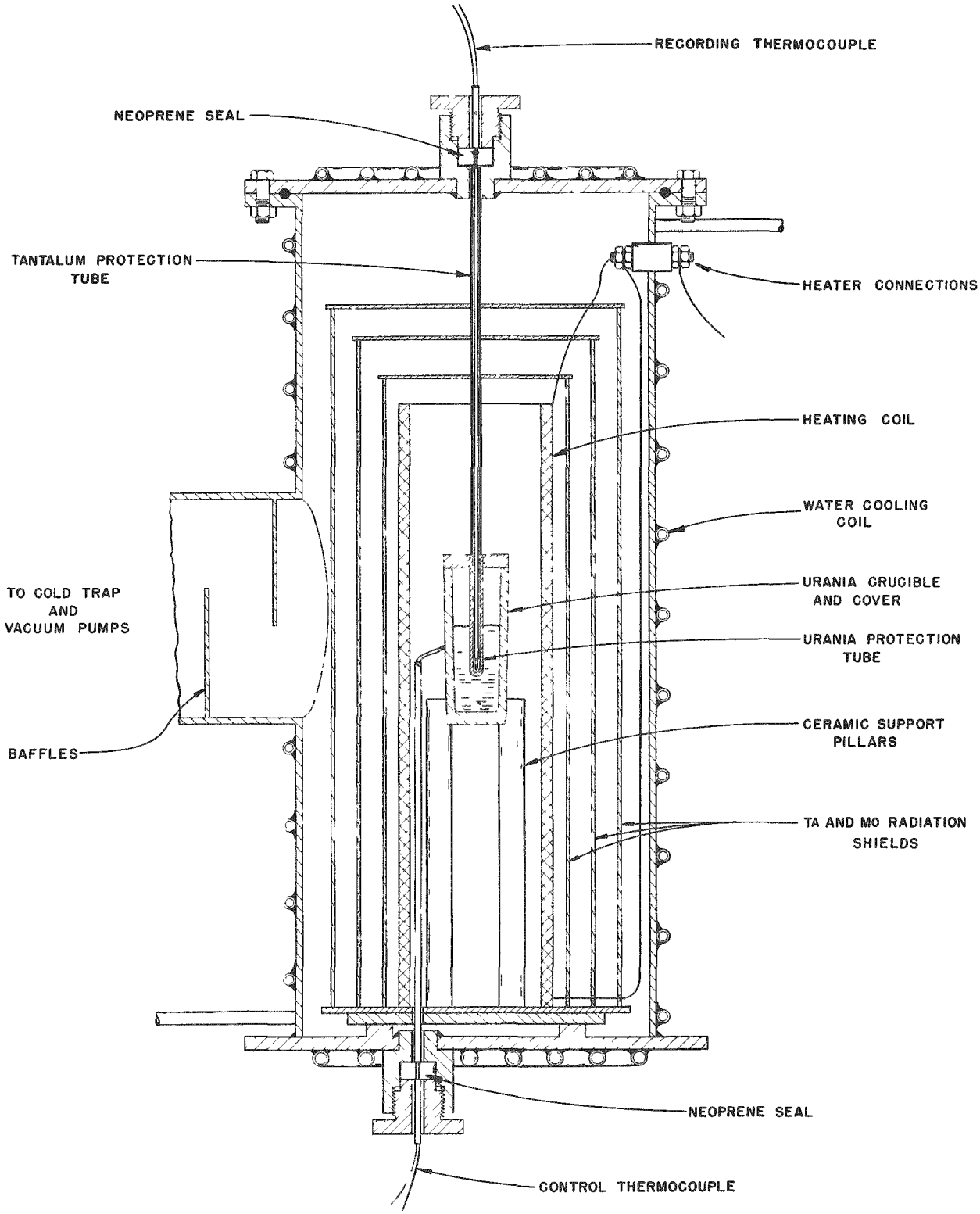

FIG.1 THERMAL ANALYSIS APPARATUS

HEAT FLOW CONTROLLED BY DIFFERENTIAL THERMOCOUPLE ARRANGEMENT

controls. The furnace was heated by two separate sets of Globars: one provided the manually adjusted base load (about two-thirds of the total) and the other the control load. The latter set of Globars was supplied with power by a Variac, which was driven by an air-operated diaphragm motor (Conoflow Corp.) in conjunction with a Minneapolis-Honeywell triple-range pneumatic controller (2 to 8, 6 to 12, and 10 to 16 millivolts). The program control was imposed by a cam cut to suit the desired cycling pattern. Since the control thermocouple was touching the outside of the furnace tube, it did not register the true temperature inside the furnace. The temperature difference due to the changing conditions of the experiments was about 25°C. To compensate for this difference, the cam was cut for a temperature that much higher. With this compensation it was possible to impart any desired temperature pattern to the specimen. Since the furnace had a low heat capacity, it followed the predetermined cycle with little lag.

For melting point determinations, a specimen of about 300 grams was contained in a urania crucible; a Pt/Pt-10% Rh thermocouple protected by a urania tube was located in its center. Great care was taken to make sure that the thermocouple remained in its central position throughout the melting and freezing cycles. The rather rigid suspension is shown in Figure 2.

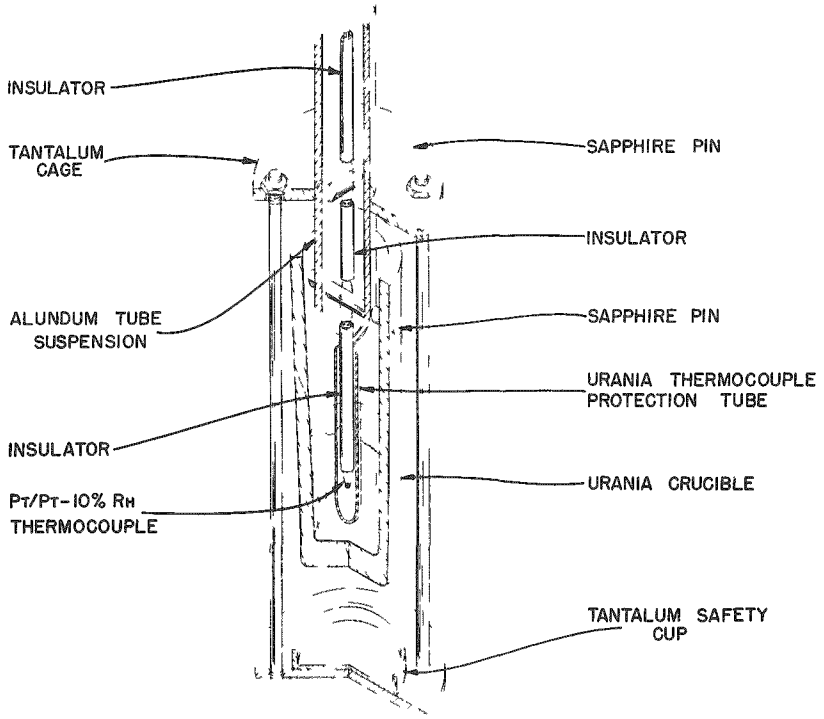

FIG 2 SUSPENSION OF CRUCIBLE FOR THERMAL ANALYSIS APPARATUS

For the solid-state transformations a similar quantity of bare metal was suspended in the furnace, as shown in Figure 3. The lead-through of the thermocouple is shown in Figure 4. The cold junctions of both the measuring and the control thermocouples were held at 0°C in well-insulated Thermos bottles. Suitable precautions were taken to shield crucible and melt from the cold sections of the furnace and to establish a uniform temperature gradient around the melt or the solid specimen.

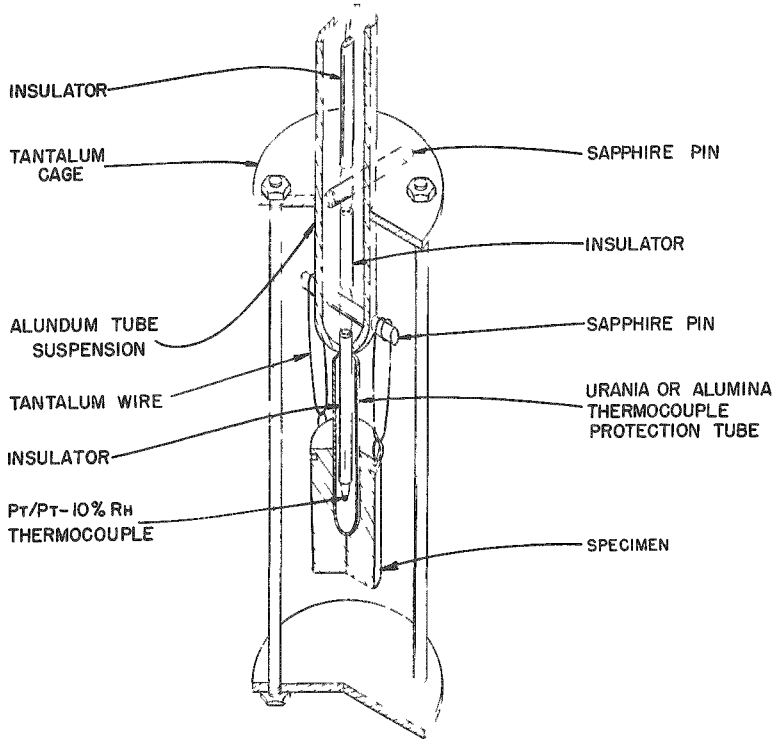

FIG 3 SUSPENSION OF SPECIMIEN FOR SOLID STATE THERMAL ANALYSIS

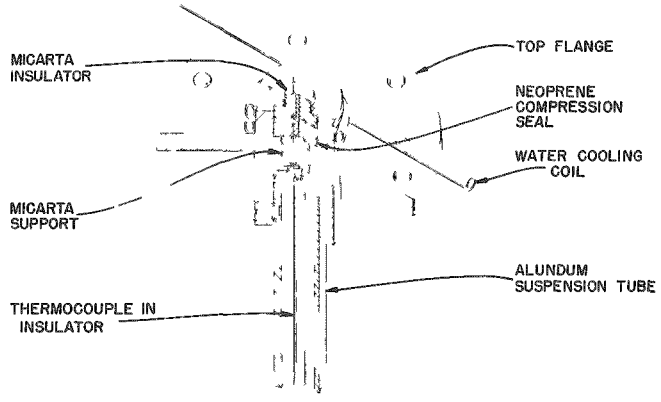

FIG 4 THERMOCOUPLE LEAD THROUGH AND ALUNDUM TUBE SUSPENSION IN THERMAL ANALYSIS APPARATUS

Despite the sensitivity of the urania refractories to thermal and mechanical stresses, the arrangement proved to be highly successful, provided the system was not cooled to room temperature during an experiment. Many cycles at various rates in the range of ± 40°C around the melting point could be made over a period of days. A pressure of 5 to 7 x 10^{-7} mm Hg was easily maintained throughout each series of cycling experiments.

The specimen temperature was recorded by a specially built Leeds and Northrup Speedomax recorder with a span of 3 millivolts and ranges beginning at 0, 2.5, 5, 7.5, and 10 millivolts. Its sensitivity was 0.003 millivolt and its error within 0.009 millivolt. The instrument was calibrated for recording of the correct millivolt value and for mechanical differences in recording at rising or falling temperatures before and after each experiment by means of a Rubicon potentiometer. In the later runs the paper position was checked by continuously tracing a straight line with a separate, fixed pen. Under these circumstances it was possible to read the voltage within ± 0.005 millivolt.

The measuring thermocouple was calibrated before and after each group of experiments over the range from 500 to 1250°C against a standard couple which had been calibrated by the National Bureau of Standards. The corrections applied to the actual temperature measurements were obtained from smoothed-out curves of these two calibrations. Care was taken to obtain a strain-free thermocouple by annealing it in air at 1500°C. Thus four corrections were applied to each individual voltage measurement: one for errors in instrument recording, a second for errors due to paper position, a third for the calibration of the measuring thermocouple against the standard couple and a fourth for the calibration of the standard couple by NBS. Ultimately, the millivolt values were converted to degrees centigrade using the tables of NBS Circular No. 561.

Occasionally a heating or cooling curve, which generally confirmed the findings of the instrument, was made by direct potentiometric measurement. Figure 5 shows a photograph of the equipment.

The dilatometer used by Lloyd for measurements of the solid-state transformation temperatures has been described previously.[19] For this investigation, the specimen thermocouple was replaced by two couples: one continued to operate the temperature recorder and the other, a calibrated chromel-alumel thermocouple, was connected to a Rubicon potentiometer via a cold junction at 0°C.

The chromel-alumel thermocouple was calibrated against a Pt/Pt-10% Rh thermocouple calibrated by the Bureau of Standards. The average deviation of the temperature indicated by the standard was -0.5°C. The appropriate corrections were applied to the measured values.

The specimens were 1 inch long by 0.200 inch in diameter with a hole 1/16 inch in diameter and 1/4 inch deep in one end to receive the thermocouples. By this means the thermocouple hot junction was prevented from "seeing" the furnace windings directly, thereby giving reasonable assurance that the temperature measured was the true temperature of the specimen at that location.

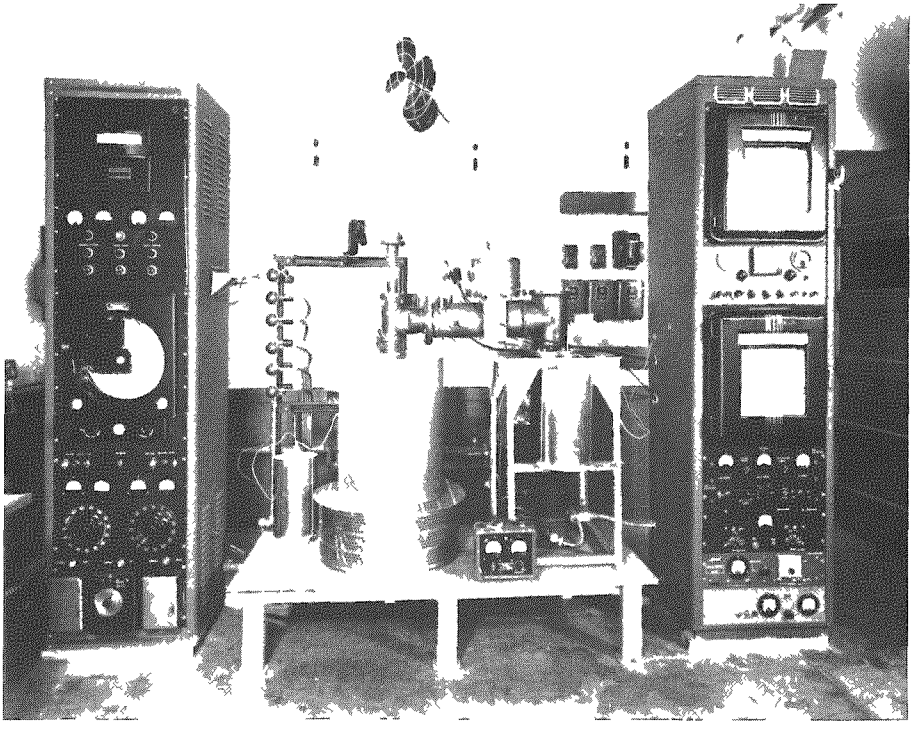

Fig. 5. Furnace and Instrumentation for Thermal Analysis

IV. DATA

A. Melting and Freezing

The data obtained by Baumrucker for the melting and freezing points are listed in Table VI. The measurements were made after the crucible and other refractories in the furnace had been outgassed in a blank run. No constant rates of heating or cooling were realized, and the rates shown in the table were those at the beginning of the transformation. Essentially no hysteresis was observed, nor was there any indication of

recalescence. In some cases the freezing point of a specimen was higher than its melting point. The mean of the data was 1131.1±0.5°C, and the standard deviation, σ, was 1.4°C.*

TABLE VI

Melting and Freezing Temperatures of High-purity Uranium at Various Rates, by Baumrucker

Specimen No.	Melting (°C)	Rate (°C/min)	Freezing (°C)	Rate (°C/min)
B-327	1130.2	0.60	1131.1	2.80
	1131.0	1.50	1131.0	1.34
	1130.5	3.04		
B-369	1130.8	3.11	1130.9	1.26
	1130.8	3.88	1130.8	0.79
B-370	1129.7	2.78	1129.4	1.18
	1129.1	3.02	1128.5	1.35
B-417	1133.7	3.16	1133.2	1.18
	1133.5	3.46	1133.2	1.13
	1132.9	3.25	1132.9	1.25
B-427	1130.5	2.02	1130.9	1.89
	1130.3	2.78	1129.8	2.60
Mean of 5 specimens	1131.1 ± 0.5 σ = 1.4*		1131.1 ± 0.5 σ = 1.4	
Mean of melting and freezing	1131.1 ± 0.5 σ = 1.4			

* Unless it is stated otherwise, the values recorded for the transformation temperatures are the arithmetical mean of the particular group of data. The value ± 0.5°C reflects the absolute accuracy of the mean transformation temperature as determined from the accuracy claimed by the National Bureau of Standards for the calibration of the primary standards used in these works. Standard deviations, σ, about the mean transformation temperature have been calculated according to the equation

$$\sigma = \frac{\sum_{i=1}^{N} |R_i|}{N} \sqrt{\frac{\pi}{2}}$$

where N is the number of observations and R_i is the difference between mean transformation temperature and the i'th observed temperature. The σ values give a measure of the precision, or reproducibility, within the particular group of data.

The data by Blumenthal are given in Table VII. The results were obtained at a constant rate of 0.74°C/min. Good arrests of about 22-minute duration were obtained during the 7 to 11 cycles which were made on each specimen. Although the graphs produced by the automatic recorder gave no indication that superheating or undercooling took place,

TABLE VII

Melting and Freezing Temperatures of High-purity Uranium at a Rate of 0.74 °C/min, by Blumenthal

Specimen No.	Melting Point (°C)	Freezing Point (°C)
B-721	1133.0 1132.3 1132.3 1131.9 1132.0 1132.5	1135.1 1134.5 1134.1 1133.8 1133.9 1133.9 1133.6
B-724	1131.8 1131.1 1130.9 1130.8 1131.4 1131.7 1131.6	1131.8 1131.3 1131.9 1131.9 1132.1 1131.8 1132.0
B-726	1130.1 1130.3 1130.6 1130.8 1130.9 1131.0 1130.7 1130.6 1130.9	1133.3 1133.3 1133.8 1133.3 1133.4 1133.4 1133.8 1132.9 1132.8 1133.6 1133.0
Mean of 3 ingots	1131.3 ± 0.5 σ = 0.8*	1133.1 ± 0.5 σ = 1.0
Mean of melting and freezing	1132.3 ± 0.5 σ = 1.3	

$$* \sigma = \frac{\sum_{i=1}^{N} |R_i|}{N} \sqrt{\frac{\pi}{2}}$$ = standard deviation of the data from the mean value

a direct potentiometric measurement on ingot B-726 showed very clearly that both effects did occur. In all cases the freezing temperatures were higher than the melting temperatures. The reason for this is not known. A possible explanation, however, is provided by the presence of a temperature gradient between the melt and the thermocouple which is shielded by rather poorly conducting refractory (urania). This temperature gradient persists through the long arrests and causes the measured temperature to be lower during heating and higher during cooling. It is reasonable to assume that the gradients are the same on heating and cooling. The mean of the melting and freezing temperature was then the equilibrium solid$\rightleftharpoons$liquid transformation point. This point was at 1132.3 ± 0.5°C and the standard deviation was 1.3°C.

The difference of 1.2°C between the mean results of Baumrucker and Blumenthal cannot be explained easily. Since the melting temperatures agreed within the limits of accuracy, the difference may be due to the difference in observed freezing temperatures. It is probable that Baumrucker missed the recalescence during solidification and that his data are too low. Since the higher temperatures agree with the earlier measurements on less pure material by Dahl and Cleaves and since generally materials of higher purity give higher equilibrium temperatures than materials of lower purity, the higher values are believed to be more nearly true than the lower ones.

B. The Alpha-Beta Transformation

Baumrucker's data are listed in Table VIII and plotted in Figure 6. Again, no constant rates of heating or cooling were realized; the rates indicated in the table and used for plotting the figure were those at the beginning of the transformation. They cover a too narrow range for a plot of arrest temperature versus rate to show a clear relationship between these two variables. The recorded heating curves did not indicate that superheating occurred at rates of up to 5°C/min. On cooling, however, a certain amount of recalescence was always present. The magnitude of the recalescence decreased only slightly with decreasing cooling rates. Slight decreases of the transformation temperatures were noted during arrests following recalescence on cooling. The hysteresis for the transformation ranged from 6.8 to 11.3°C, with an average near 8.7°C.

The very large hysteresis between heating and cooling, even at low rates, and the large effect of the rate on the magnitude of this hysteresis made a new approach to the determination of the solid-state transformation points mandatory. A few direct potentiometric measurements showed clearly that not only undercooling, but also superheating, were real. Furthermore, it was not at all sure that upon recalescence the latent heat

TABLE VIII

Alpha-Beta Transformation Temperatures of High-purity Uranium at Various Rates of Heating and Cooling, by Baumrucker

Specimen No.	$\alpha \rightarrow \beta$ (°C)	Rate (°C/min)	$\beta \rightarrow \alpha$ (°C)	Rate (°C/min)
B-327	666.7 667.0	1.20 1.40	656.4 655.7	1.90 1.53
B-369	666.0 666.4 666.3	1.03 2.03 1.35	656.5 656.5	1.24 1.68
B-370	665.5 665.8 666.8 666.6	1.25 1.10 1.59 2.03	657.9 659.0 658.8 658.5	0.97 0.83 1.35 1.12
B-417	667.2 667.2 667.4 667.5 667.2	1.09 1.21 1.45 1.49 1.42	659.1 659.0 658.1 658.5 658.4	1.18 1.10 1.26 1.15 1.19
B-427	667.6 666.9 667.1	1.86 1.48 1.62	659.5 658.9 658.3 658.3	0.72 0.70 1.25 1.24
Mean of 5 Specimens	666.8 ± 0.5 σ = 0.6*		658.1 ± 0.5 σ = 1.1	

* $\sigma = \dfrac{\sum_{i=1}^{N} |R_i|}{N} \sqrt{\dfrac{\pi}{2}}$ = standard deviation of the data from the mean value.

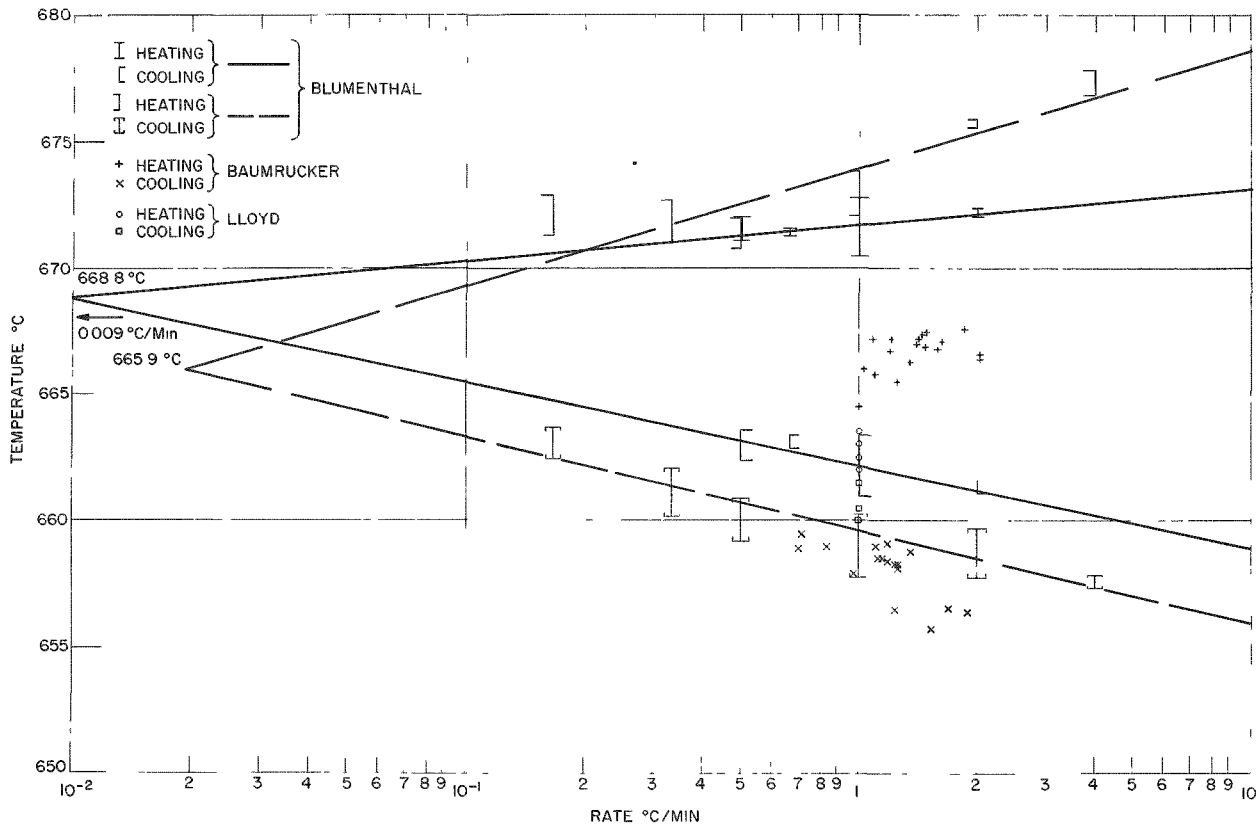

Fig. 6. Effect of Heating and Cooling Rate on the $\alpha \rightleftharpoons \beta$ Transformation Temperature of High-purity Uranium

evolved brought the specimen temperature back to the equilibrium temperature. Lag in the response of the temperature-sensing element was still another factor to be considered.

Blumenthal, therefore, approached the problem by measuring the transformation temperatures on heating and cooling at various constant rates. The spread between heating and cooling of the $\alpha \rightleftharpoons \beta$ transformation temperature decreased as the rate decreased. A plot of the mean transformation temperature for a given cooling rate versus the logarithm of the rate shows that the present data form a satisfactory continuation of Duwez'[4] data for high-purity uranium obtained at much higher cooling rates (Figure 8).

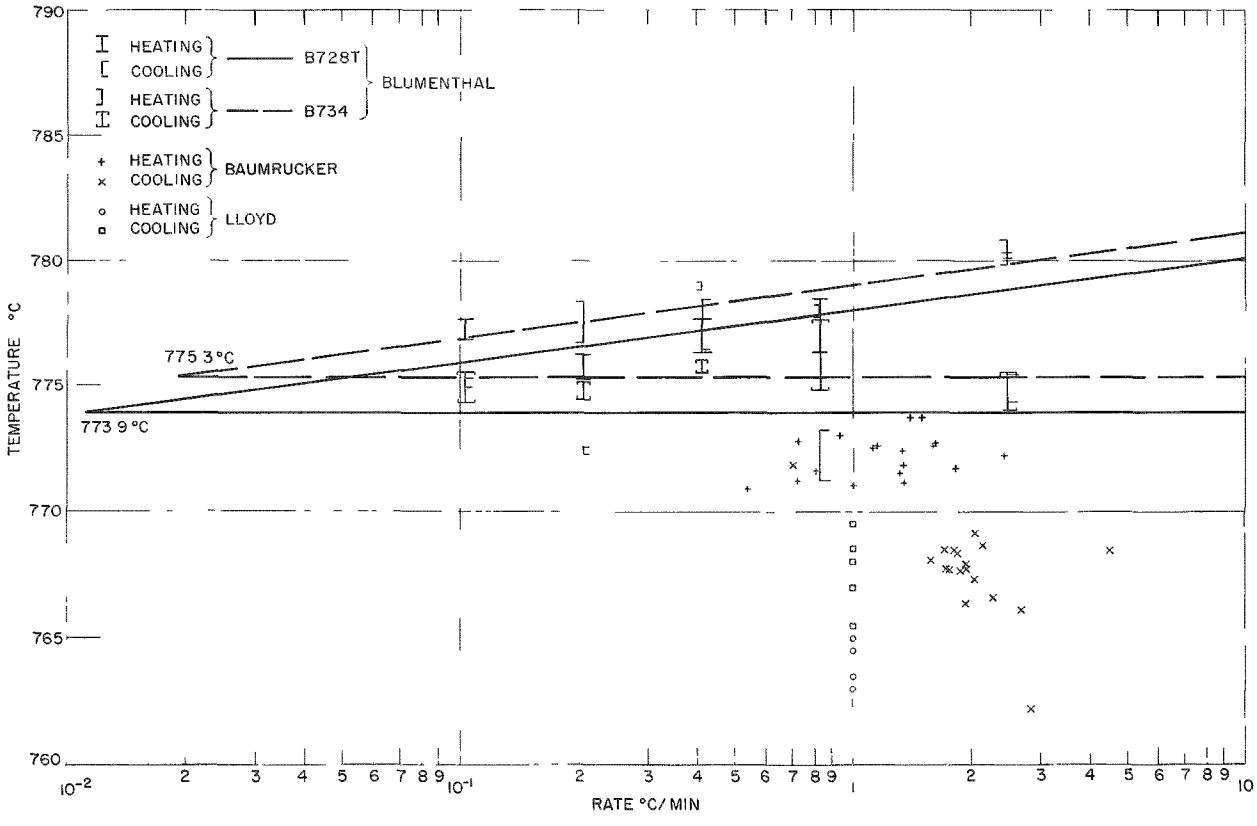

Fig. 7. Effect of Heating and Cooling Rate on the $\beta \rightleftharpoons \gamma$ Transformation Temperature of High-purity Uranium

The left end of the curve may be regarded as a straight line. Based on this assumption, the data may be fitted by least mean square analyses to functions of the type

$$T_H = a_1 + b_1 \log r$$

$$T_C = a_2 - b_2 \log r \quad ,$$

where T_H and T_C are the transformation temperatures in °C on heating and cooling, respectively, log r is the decadic logarithm of the rate, and a_1, a_2, b_1 and b_2 are constants. The two lines represented by these equations intersect at the temperature $T = T_H = T_C$ which is the temperature where the disturbing factors of hysteresis, superheating and undercooling disappear and which may be regarded as the equilibrium temperature of the transformation under investigation. By this method, the following equations and transformation temperatures were obtained:

For $\alpha \rightleftharpoons \beta$ (Ingot B-724)

$$T_H = 671.74 + 1.436 \log r, \ \sigma = 0.69°C*$$

$$T_C = 662.19 - 3.263 \log r, \ \sigma = 0.76°C \ .$$

The two lines intersect at T = 668 8 ± 0.5°C and at r = 0.009°C/min. This somewhat slower rate was the result of the metal having been contained in a urania crucible, a procedure that was subsequently abandoned. Afterwards only bare specimens were used

For $\alpha \rightleftharpoons \beta$ (Ingot B-728T)

$$T_H = 673.95 + 4.679 \log r, \ \sigma = 0.97$$

$$T_C = 659.62 - 3.695 \log r, \ \sigma = 0.76 \ .$$

The two lines intersect at T = 665.9 ± 0 5°C and at r = 0.019°C/min. The mean of the two values is 667.4 ± 0.5°C The details of Blumenthal's measurements are given in Table IX and the extremities of the data are plotted in Figure 6. Baumrucker's mean value 666.8 ± 0.5 for heating agrees with this value within the limits of accuracy.

C. The Beta-Gamma Transformations

Baumrucker's data for the $\beta \rightleftharpoons \gamma$ transformation are listed in Table X and plotted in Figure 7 The experimental conditions were the same as in the $\alpha \rightleftharpoons \beta$ case. Recalescence for the $\gamma \rightarrow \beta$ transformation was smaller than for the $\beta \rightarrow \alpha$ transformation, but recalescence was more susceptible to diminution with decreasing cooling rates for $\gamma \rightarrow \beta$ than for $\beta \rightarrow \alpha$. The hysteresis for the $\beta \rightleftharpoons \gamma$ transformation was smaller than for the $\alpha \rightleftharpoons \beta$ transformation. The range of the hysteresis for $\beta \rightleftharpoons \gamma$ was from 1.9°C for a low rate to 9.4°C for a higher rate.

Blumenthal's extrapolation method, which was described above for the $\alpha \rightleftharpoons \beta$ transformation, also was applied to the $\beta \rightleftharpoons \gamma$ transformation temperature data (Table XI and Figure 7). The two specimens (B-728T and B-734) underwent superheating in a manner comparable to that observed for the $\alpha \rightarrow \beta$ transformation

*σ in this and similar cases gives the standard deviation of the data from the least mean square fitted equations.

TABLE IX

Alpha-Beta Transformation Temperatures of High-purity Uranium at Various Rates of Heating and Cooling, by Blumenthal

Rate (°C/min)	Specimen B-724		Specimen B-728T	
	$\alpha \rightarrow \beta$ (°C)	$\beta \rightarrow \alpha$ (°C)	$\alpha \rightarrow \beta$ (°C)	$\beta \rightarrow \alpha$ (°C)
4.00			677.9 677.0 676.9	657.8 657.4 657.9
2.00	672.1 672.4 672.4	661.6 661.3 661.1	675.9 675.8 675.9 675.7 675.9 675.6 675.7 675.7	659.4 659.7 658.7 657.8 657.9 658.1 658.5 658.0
1.00	672.5 672.3 671.3 672.6 672.8 670.5 671.0 671.1 670.9	663.0 662.7 662.0 663.0 663.4 661.1 661.3 661.0 661.0	673.9 672.1 672.1 672.1	660.1 660.3 659.4 657.8
0.667	671.5 671.3	663.4 663.0 663.0 662.9		
0.50	671.1 672.0	662.4 663.6	670.8 672.0 672.0	659.2 660.9
0.333			672.7 671.4 671.0 671.7	661.5 661.9 662.0 660.2
0.167			671.3 672.9	662.5 663.7

TABLE X

Beta-gamma Transformation Temperatures of High-purity Uranium at Various Rates of Heating and Cooling, by Baumrucker

Specimen No.	$\beta \rightarrow \gamma$ (°C)	Rate (°C/min)	$\gamma \rightarrow \beta$ (°C)	Rate (°C/min)
B-327	773.7 773.7 773.0	1.40 1.50 0.93	771.8 768.6	0.70 2.14
B-369	771.2 771.6 771.1	0.72 0.80 1.03	767.7 762.2 766.1	1.77 2.86 2.69
B-370	771.0 770.9 771.8 772.2 771.7	1.00 0.54 1.34 2.43 1.83	767.7 768.4 768.0 766.6 767.7	1.95 4.50 1.58 2.27 1.72
B-417	772.8 772.6 772.5 772.7 772.6	0.73 0.87 1.12 1.62 1.59	769.1 768.4 768.3 766.4 767.9	2.04 1.81 1.85 1.94 1.94
B-427	772.4 771.5	1.34 1.31	768.4 767.6 767.3	1.71 1.87 2.03
Mean of 5 specimens	772.2 ± 0.5 σ = 0.9*		767.7 ± 0.5 σ = 1.4	

* $\sigma = \dfrac{\sum_{i=1}^{N} |R_i|}{N} \sqrt{\dfrac{\pi}{2}}$ = standard deviation of the data from the mean value

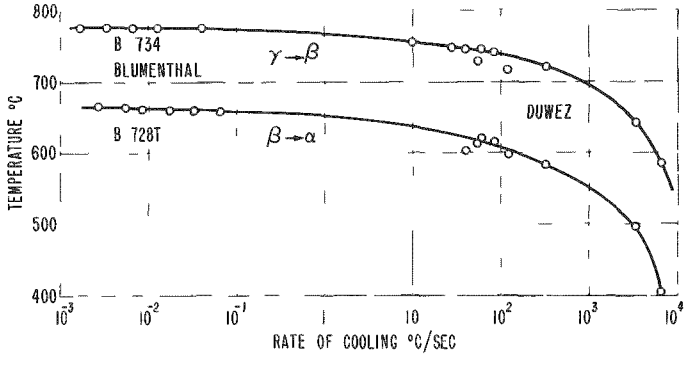

Fig. 8. Effect of Cooling Rate on the $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ Transformation Temperatures of High-purity Uranium (At left data by Blumenthal, at right data by Duwez)

TABLE XI

Beta-gamma Transformation Temperatures of High-purity Uranium at Various Rates of Heating and Cooling, by Blumenthal

Rate (°C/min)	Specimen B-728T		Specimen B-734	
	$\beta \rightarrow \gamma$ (°C)	$\gamma \rightarrow \beta$ (°C)	$\beta \rightarrow \gamma$ (°C)	$\gamma \rightarrow \beta$ (°C)
2.47	780.1 780.1 780.3	774.4 774.3 775.4	780.8 780.6 780.1 779.8	774.0 774.7 775.5 775.5
0.825	778.4 777.7 777.6 777.1 777.1 777.0 776.4 776.3	773.2 773.0 772.8 772.2 772.2 771.7 771.7 771.2	778.0 778.1 777.7 778.1 778.0 778.2	777.5 777.6 775.2 774.8 775.8
0.412	777.6 777.3 776.3	778.4 778.0 776.4	779.1 779.1 778.8	775.5 775.9 776.0
0.206	775.5 776.2 775.2	772.3 772.5 772.5	776.9 776.7 778.3 778.3	775.0 775.1 774.5 774.4
0.103	776.8 777.6 777.5	775.3 774.9 775.0	776.8 776.9 777.0	775.5 774.3 774.6
Mean of all 5 rates		773.9 ± 0.5 σ = 2.2*		775.3 ± 0.5 σ = 0.9

$$*\sigma = \frac{\sum_{i=1}^{N} |R_i|}{N} \sqrt{\frac{\pi}{2}}$$ = standard deviation of data from the mean value

The transformation temperatures on heating versus the logarithm of the rate were again expressed by the relationship $T_H = a_1 + b_1 \log r$:

B-728T. . . . . $T_H = 778.00 + 2.095 \log r$, $\sigma = 1.16°C$

B-734 . . . . . $T_H = 778.99 + 2.148 \log r$, $\sigma = 0.86°C$.

No rate effect of the kind that was observed for the $\beta \rightarrow \alpha$ transformation took place on cooling, although recalescence was noted in several, but not all, cycles. Thus, the cooling data are best represented by the mean of the observed values which graphically form a straight line parallel to the log r axis. The intersection of the lines for heating and cooling and, therefore, the equilibrium transformation temperature were identical with the mean of the cooling data. They are (see Figure 8):

B-278T. . . . . T_C = 773.9 ± 0.5°C, σ = 2.2°C

B-734 . . . . . T_C = 775.3 ± 0.5°C, σ = 0.9°C .

The average $\beta \rightleftharpoons \gamma$ transformation temperature of the two high-purity uranium samples was 774.6 ± 0.5°C. This temperature is approximately 7°C higher than the mean of Baumrucker's cooling data, most of which were obtained at rates of 1.6°C/min and higher. Only one of his measurements was made at a rate of 0.7°C/min; in this case, the transformation point was only 2.8°C lower than Blumenthal's mean of 774.6°C.

It is possible that the tantalum protection tube (Figure 1) used by Baumrucker was a source of difficulty. It may have contributed to heat conduction away from the thermocouple junction. It is therefore concluded that the higher value of 774.6 ± 0.5°C represents the $\beta \rightleftharpoons \gamma$ equilibrium transformation temperature.

D. Dilatometric Measurements

In the dilatometric measurements by Lloyd, the specimens were first brought to a temperature of approximately 600°C in about five minutes. The heating rate was decreased to 1.0 ± 0.1°C/min and continued until a temperature of approximately 815°C was reached. The cycle was then reversed and the specimen was slowly cooled at the same rate to a temperature below the $\beta \rightleftharpoons \alpha$ transformation.

Throughout the tests the plots of expansion versus temperature were recorded automatically. The temperatures of transformation were taken as those temperatures, measured manually by the calibrated chromel-alumel thermocouple and a Rubicon potentiometer, at which a sudden change of slope occurred in the curve of expansion versus temperature. In all cases the change of slope was quite distinct and left no doubt as to the temperature at which the transformation began.

Figures 9 and 10 show a typical expansion curve for 300°C rolled material (Run 63). Each major division of the ordinate (1/3 inch on recording graph) is equal to 2.85 x 10^{-4}-inch expansivity and each numbered division of the abscissa equals 1 millivolt (Pt/Pt-10% Rh thermocouple).

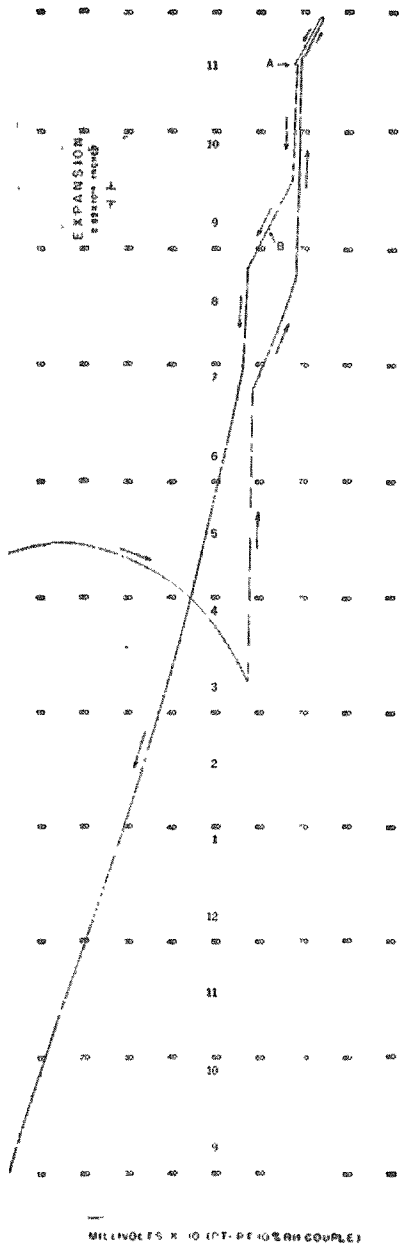

Fig. 9. Expansion Curve of High-purity Uranium (B-272-3a; Run 63)

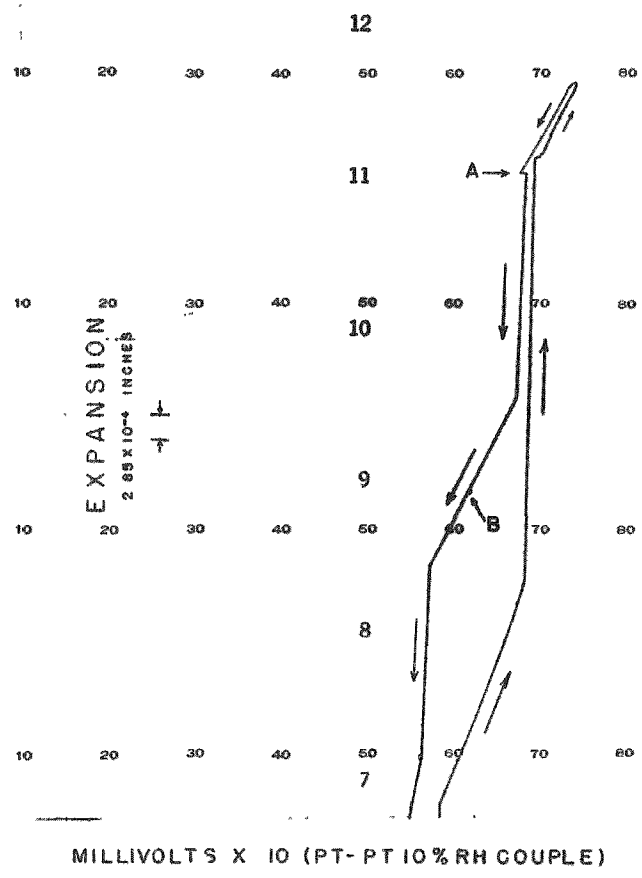

Fig. 10. Portion of Expansion Curve of High-purity Uranium (B-272-3a, Run 63). The curve shows, at point A, recalescence in $\gamma \rightarrow \beta$ transformation and, at point B, heat evolution in β region.

Figure 9 shows the initial expansion followed by contraction in the alpha temperature range, which is characteristic of a direction parallel to the rod axis for material rolled or swaged in the alpha-phase low temperature range. At the start of the $\alpha \rightarrow \beta$ transformation a very sharp change occurred in the direction of the expansion curve. The temperature of the specimen continued to rise slightly during the transformation because of continued heat input. At the end of the transformation, the curve changed

its slope and continued to indicate uniform expansion in the beta phase. The change in slope at the start of the $\beta \longrightarrow \gamma$ transformation again was abrupt. Heating was continued into the gamma region to allow establishment of a uniform rate of cooling before the beginning of the $\gamma \longrightarrow \beta$ transformation.

The start of the $\gamma \longrightarrow \beta$ transformation showed a sharp recalescence of approximately 8°C (see Figure 10, point A). The temperatures recorded are those to which the specimen rose after the recalescence. The start of the $\beta \longrightarrow \alpha$ transformation was also characterized by recalescence, which was of smaller magnitude (less than 0.5°C); it was sufficiently large to be picked up by the potentiometer, but did not show on the recorded expansivity curve.

The results of seven runs for high-purity uranium are given in Table XII and plotted in Figures 6 and 7. The temperatures are recorded to the nearest 0.5°C. The interesting result of these measurements is the agreement with Blumenthal's thermal analytical data on cooling for the $\beta \longrightarrow \alpha$ transformation at a comparable rate. In the case of $\gamma \longrightarrow \beta$, the dilatometric transformation temperature is about 4°C lower than the thermally obtained temperature. Since the temperature continued to drop during the transformation, it is quite probable that the recalescence did not bring the specimen temperature back to its equilibrium value. Because undercooling and recalescence are small in the $\beta \longrightarrow \alpha$ case, the agreement with the thermal results is good.

TABLE XII

Dilatometric Transformation Temperature Measurements on High-purity Uranium at a Rate of 1°C/min, by Lloyd

Spec No.	Run No.	Prior Mechanical and Thermal Treatment *	Transformation Temperatures (°C)				Temperature (°C) at which Heat Evolution was Observed on Cooling
			$\longrightarrow \rho$	$\rho \longrightarrow \alpha$	$\beta \longrightarrow \gamma$	$\gamma \longrightarrow \beta$	
B-272-1	69	Slow β annealed	663.0	660.5	764.5	768.0	728
-2	64	Slow β annealed	663.5	660.0	763.0	768.5	698
-3a	63	α swaged	662.0	660.5	763.5	768.5	690
-3b	67	Water quenched from 1000°C	662.5	660.0	763.5	767.0	672
-3b	68	β annealed	664.5	660.0	765.0	765.5	672
B-183	65	α rolled	662.0	660.0	763.0	768.5	701
	66	β annealed	662.0	661.5	765.0	769.5	686
Mean			662.8 $\sigma = 0.9$**	660.4 $\sigma = 0.5$	763.9 $\sigma = 1.0$	767.9 $\sigma = 1.2$	

* All rolling and swaging carried out at 300°C

** $\sigma = \dfrac{\sum_{i=1}^{N} |R_i|}{N} \sqrt{\dfrac{\pi}{2}}$ = standard deviation of data from the mean value

On heating, the discrepancy between the dilatometric and thermal data is substantial, being about 10°C for the $\alpha \rightarrow \beta$ transformation and about 14°C for the $\beta \rightarrow \gamma$ transformation. Moreover, the dilatometric $\beta \rightarrow \gamma$ transformation temperature is lower than the dilatometric $\gamma \rightarrow \beta$ transformation temperature, which indicates that, particularly during heating, heat transfer and heat conduction problems greatly influence these measurements. Heat transfer to the specimen may have been affected by the quartz sleeve surrounding the specimen, and heat conduction from the specimen may have been caused by the four thermocouple wires leading from the specimen. The difference between the two rates explains the observed phenomena. During cooling at the higher $\gamma \rightarrow \beta$ temperature, the heat conduction of the thermocouple wires was probably the only disturbing influence; during heating, however, the insulating effect of the sleeve was large enough to make the heat loss through the thermocouple wire more apparent.

That purity is a factor, yet not necessarily a major one, is shown in Table XIII, where the dilatometric measurements on reactor-grade uranium and remelted biscuit metal are listed. The impurity effect on the $\beta \rightarrow \alpha$ transformation is large enough to be reckoned with; in all other cases the impurity effect is relatively small, though not negligible.

TABLE XIII

Dilatometric Transformation Temperature Measurements of Impure Uranium at a Rate of 1°C/min, by Lloyd

Spec. No.	Run No.	Material	Prior Mechanical and Thermal Treatment*	Transformation Temperatures (°C)				Temperature (°C) at which heat evolution was observed on Cooling
				$\alpha \rightarrow \beta$	$\beta \rightarrow \alpha$	$\beta \rightarrow \gamma$	$\gamma \rightarrow \beta$	
B4-1b	61	Reactor-	α rolled	661.5	652.5	764.0	767.0	660
B4-1b	62	grade	β annealed	660.0	652.5	763.0	767.0	661
B4-1c	70	Uranium	α rolled	660.5	752.0	763.0	765.5	678
B4-1d	71		α rolled	661.5	651.5	763.5	765.5	none
		mean		660.9	652.1	763.4	766.2	
B-246a	73	Remelted	α swaged	660.0	654.5	764.0	767.5	716
B-246b	74	Biscuit	α swaged	659.5	655.5	762.5	769.0	none
B-246c	75	Uranium	α swaged	660.5	658.0	763.5	768.5	692
		mean		660.0	656.0	763.3	768.3	

*All rolling and swaging at 300°C

E. A Beta-phase Anomaly

An anomaly encountered during the dilatometric measurements merits mention. A heat evolution was noted in the beta region on cooling (Figure 10, point B). For the high-purity specimens this occurred at temperatures ranging from 686 to 728°C (Table XII); it also occurred in several of the runs made with impure materials (Table XIII). The phenomenon was characterized by a sudden increase in temperature, resulting in a momentary slight expansion of the specimen, but with no change in the slope of the cooling curve. A similar break in thermal analysis cooling curves and in one heating curve has been reported by Duwez.[14] Other investigators have reported a break in the magnetic susceptibility curve of uranium at about 698°C.

In spite of a diligent search, neither Blumenthal nor Baumrucker were able to detect any such anomaly in their thermal analysis curves. Since Blumenthal and Baumrucker used cast material of large grain size, whereas Lloyd and Duwez used fabricated material of much smaller grain size, it is possible that the effect is associated with the release of some strain energy introduced during the $\gamma \rightarrow \beta$ transformation. It is felt that the effect merits further investigation.

V. CONCLUSION

Because of the sensitivity of the solid-state transformation to the rate at which measurements are made and because of the large effect which heat transfer and heat conduction phenomena have on the temperature measurements of all uranium transformations, only those measurements should be considered valid which take these factors into account. It is, therefore, felt that Blumenthal's data are the closest to the true equilibrium values. His results for the mean transformation temperatures of high-purity uranium are

$\alpha \rightleftharpoons \beta$: 667.4 ± 0.5°C

$\beta \rightleftharpoons \gamma$: 774.6 ± 0.5°C

$\gamma \rightleftharpoons L$: 1132.3 ± 0.5°C

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