Heat Content of Zirconium and of Five Compositions of Zirconium Hydride from 0° to 900° C [1]

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Using a precise Bunsen ice calorimeter, a "silver core" furnace, and a "drop" method, the heat content (enthalpy) of zirconium metal and five samples of zirconium hydride (24 to 52 atomic percent hydrogen) was measured over the range 0° to 900° C. Thermal hysteresis of the hydrides was investigated in several cases, and corrections were applied for the impurities in the samples. At each temperature up to 550° C the heat contents of the hydrides relative to 0° C were found to vary linearly with composition, a fact in accord with the phase diagram of the system. The effective heat capacity of each hydride sample reached its maximum value between 550° and 600° C, a behavior that can be interpreted as due to the endothermic formation of the high-temperature beta phase.

1. Introduction

The fact that palladium metal absorbs considerable amounts of hydrogen gas has been known for a very long time. Although many metals form similar alloylike solid hydrides, those of the family of chemical elements titanium, zirconium, hafnium, and thorium have become well known because of their ease of formation, wide ranges of composition, and relative stability. In the case of zirconium no gaseous hydrides are known, but the metal expands and absorbs continuously variable amounts of hydrogen even at room temperature, forming brittle, metalliclike materials whose compositions approach ZrH_2. Only those with the largest amounts of hydrogen have decomposition pressures that exceed 1 atm below 1,000° C.

Many of the physical properties of the zirconium hydrides have been investigated intensively, especially in recent years. These properties include their crystal structures as determined by X-ray and neutron diffraction, their paramagnetic susceptibilities, and the diffusion rates and equilibrium pressures of hydrogen at various temperatures and compositions. This paper reports an extensive series of measurements of the heat content of zirconium and five compositions of its hydrides from 0° to 900° C.

2. Samples and Their Compositions

The samples of zirconium hydride whose heat contents were measured are listed in table 1 in the order of increasing hydrogen content. Their compositions, corrected for chemical impurities in the manner presently to be described, are expressed in several forms that are commonly used. Zirconium metal is included with the hydrides, as it is a member of the series not only in a formal sense but also in terms of its properties. The zirconium sample was crystal-bar material, and was obtained from the U. S. Bureau of Mines, Albany, Oregon.

In the case of pure zirconium hydrides the three ways of expressing the hydrogen content used in

TABLE 1. *Samples and their compositions*

Sample	Source of sample	Composition		
		Weight % H (w)	Atom % H (A)	Atomic ratio H/Zr (x)
1	U. S. Bureau of Mines	0.000	0.0	0.000
2	Wright Air Dev. Ctr	.356	24.5	.324
3	Sylvania	.611	35.7	.556
4	do	.769	41.2	.701
5	do	1.092	50.0	.999
6	Wright Air Dev. Ctr	1.170	51.7	1.071

table 1 are related to one another, and to the hydrogen as parts per million by weight (ppm), by the following numerical formulas. (The symbols are defined in table 1.)

$$ppm=10{,}000w=110.5A/(1-0.00989A)=11{,}050x/(1+0.01105x) \quad (1)$$

$$A=90.50w/(1+0.895w)=100x/(1+x) \quad (2)$$

$$x=0.905w/(1-0.01w)=A/(100-A). \quad (3)$$

The methods used in preparing the hydride samples were as follows: Samples 2 and 6 were prepared by the Power Plant Laboratory of the Wright Air Development Center. The zirconium used had been prepared by the Carborundum Metal Corporation. The hydriding temperature was 1,800°F (982°C), and a period of 2 hr was allowed in order to preclude temperature gradients along the bar. The furnace was shut down thereafter and the bar cooled in the furnace for at least 8 hr. The percentages of hydrogen furnished with the samples were determined by the manufacturer by three different methods, described as vacuum fusion, weight gain, and volumetric analysis. The three methods agreed very closely, and the estimated accuracy was stated to be of the order of 0.5 percent of the hydrogen present. Samples 2 and 6 were each supplied in two pieces, which were measured as a single sample to increase the precision, as in each case both pieces were stated to have the same composition and were found to have room-temperature densities that were identical within the uncertainty of measurement.

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Samples 3, 4, and 5 were supplied by Sylvania Electric Products, Inc., Atomic Energy Division. It was stated that at the time of their preparation only a commercial grade of zirconium was available. The metal was heated to 920°C, and exposure to hydrogen gas was then begun. As the system slowly cooled (reaching 800°C in about 45 min), the pressure of hydrogen was maintained equal to the equilibrium pressure of the solid phase down to 0.2 atm. No further adjustments of pressure were made during the subsequent slow cooling overnight to room temperature, because it was believed that changes in the composition of the solid during this time were insignificant. It was stated that the greatest difference in temperature in any one sample did not exceed 4 deg C. Tests for homogeneity were not made on these particular samples, but were on others, which showed no composition differences within the accuracy of analyzing for hydrogen. The compositions of samples 3, 4, and 5 given in table 1 are based on analyses at Sylvania Electric Products, Inc., using a combustion method. Additional specimens that were approximate duplicates of these three compositions also were supplied. No heat-content measurements were made on them, but the parallel specimens were ground to a particle size of 60 to 100 mesh and were analyzed at the National Bureau of Standards for carbon and hydrogen by a combustion method. The hydrogen contents thus found differed from the values reported by Sylvania by amounts that, expressed as percentages of the hydrogen present, varied from −1.5 to +3 percent.

The chemical impurities found by analysis in the six samples are given in detail in table 2. These values were obtained by qualitative spectrographic analysis, except where otherwise indicated, and presumably no value was determined where none is listed. Samples 3, 4, and 5 themselves were not analyzed for carbon, but the value given is probably approximately correct, as it is the mean of those found (0.29 to 0.35%) for the duplicates of these samples.

TABLE 2. *Impurities in the zirconium hydride samples*

(Percentage by weight)

Element	Sample—					
	1	2	3	4	5	6
Hf	0.0145	0.01	[a] 0.60	[a] 0.44	[a] 0.48	0.01
Fe	.030	.1	[a] .88	[a] .53	[a] .41	.1
C	[b] .02	[b] .06	[b] .32	[b] .32	[b] .32	[b] .06
N	[b] .005	[b] .01	------	------	------	[b] .01
O	[b] .006	[b] .017	------	------	------	[b] .017
Si	<.002	------	[a] .48	[a] .35	[a] .34	------
Ni	.002	.007	[a] .04	[a] .08	[a] .07	.007
Cr	<.001	.01	[a] .10	[a] .06	[a] .06	.01
Al	.00025	.01	[a] .12	[a] .12	[a] .17	.01
Mn	<.001	.01	[a] <.01	[a] <.01	[a] <.01	.01
Ti	.0035	------	[a] .06	[a] <.01	[a] <.01	------
Pb	<.001	.005	[a] .03	[a] <.01	[a] <.01	.005
Mg	.001	.005	<.01	<.01	<.01	.005
Sn	<.0005	.005	<.001	<.01	<.01	.005
Be	------	.0001	------	------	------	.0001
V	<.002	.005	<.0001	<.0001	<.0001	.005
Ag	------	------	<.001	<.001	<.001	------
Ca	------	------	<.01	<.01	<.01	------
Cu	.001	------	<.01	<.01	<.01	------
Zn	<.005	------	------	------	------	------
Cd	<.00005	------	<.0001	<.0001	<.0001	------
B	.00005	------	<.0001	<.0001	<.0001	------
Mo	<.001	------	<.0001	<.0001	<.0001	------
Co	<.0005	------	<.0001	<.0001	<.0001	------
Total %	0.09	0.25	2.6	1.9	1.9	0.25

[a] By quantitative spectrographic analysis. [b] By chemical analysis.

The method of correcting the hydrogen compositions for the impurities shown by analysis is consistent with the method of correcting the thermal values described later, and was as follows: The total mass of those impurities whose small atomic sizes indicate clearly that they must be interstitial instead of substitutional in the zirconium lattice (carbon, nitrogen, and oxygen) were subtracted from the total sample mass. The remaining impurities were then assumed to be replaced atom for atom by zirconium before recalculating a corrected sample mass and a corrected percentage by weight of hydrogen.

3. Measurements of Heat Content

The calorimetric apparatus and method used have been described in critical detail in several reports and papers of the Bureau during the past 10 years [1].[2]

In the heat-content measurements the sample was contained in a thin-walled cylinder of the alloy 80Ni-20Cr sealed by a gold gasket. The hydride samples were not clad with any protective coating to prevent the escape of hydrogen, for in the worst case (at 900° C and 1-atm pressure of hydrogen) the 4 cm^3 of gas space in the container will hold only 0.08 mg of hydrogen gas, and this is only about 0.04 percent of the total hydrogen in the sample used. Small losses in mass attributed to loss of hydrogen did occur at the highest temperatures (800° C and above), as discussed later, but these aggregate losses equaled only a small fraction of the hydrogen in the solid sample. As the container appeared to remain sealed in most cases, these losses of hydrogen presumably occurred by diffusion through the container walls.

Briefly, the method of heat measurement was as follows: The specimen and container were suspended in the furnace for sufficient time to ensure their reaching the known constant temperature of the furnace, which was always adjusted to a rounded value. They were then allowed to fall into a precision Bunsen ice calorimeter, which, by absorbing mercury equivalent in volume to the shrinkage caused by the melting of ice, measured the heat evolved by the sample and container in cooling to 0° C. A similar measurement on the empty container at the same furnace temperature provided correction for the heat the container itself contributed and for the small amount of heat lost during the fall into the calorimeter. The furnace temperature was measured by a calibrated platinum-rhodium thermocouple, and below 650° C also by a calibrated platinum resistance thermometer to increase the accuracy and guard against any otherwise unknown

[2] Figures in brackets indicate the literature references at the end of this paper.

shift in the calibration of either the thermometer or the thermocouple. Before being sealed, the sample container was filled with pure helium gas, which also flowed through calorimeter and furnace cores during the measurements. This minimized the times required to reach thermal equilibrium and the oxidation of the container surfaces.

The heat leak of the calorimeter is normally small and quite constant, averaging only several tenths of a calorie per hour. In many of the measurements on the zirconium hydrides, particularly those with the highest hydrogen contents, the sample continued to evolve heat in the calorimeter (up to a total of 1 cal extra) for as long as 1½ hr beyond the 20 min normally required for reaching thermal equilibrium. This slow evolution of heat was presumably due to a slow approach to final phase equilibrium, and was taken into account when the precision of the measurements seemed to justify doing so. One of the authors has used the heat-content data reported in this paper to derive, by two independent methods, the shape of one of the boundaries of the zirconium-hydrogen phase diagram (the hydrogen-rich α boundary) from 0° to 550° C. The approximate agreement of the results, using the two methods, is evidence that in this temperature range approximate phase and thermal equilibrium were obtained in the present heat-content measurements [2].

The basic heat-content data obtained are given in detail in tables 3 to 8. Heat is expressed in calories (1 cal=4.1840 absolute joules). The second column indicates the relative chronological order of the individual runs with the sample, so that the effect of intervening exposure of the sample to other temperatures may be traced.

Each value recorded in the sixth column for the heat found for the empty container is the mean for two or more measurements at the particular furnace temperature, with the following exception. The heat content of the empty container was measured several times during the series of measurements, but only at 100-deg-C intervals from 100° to 900° C (and also at 550° C), and the values for all other temperatures were found from smooth plots of the deviations from simple monotonic empirical functions of temperature. In the present case, such interpolation led to errors less than those caused by the zirconium hydride samples themselves, although in the case of samples capable of being measured with the highest precision, this procedure would hardly be accurate enough. Different values for the empty container at the same temperature arose when in cases of emergency a new container or container part had to be substituted.

The tabulation "corrections for losses of H_2" that had occurred during exposure of the sample to the highest temperatures were made on an empirical basis, being estimated from the drift of heat values from run to run at the same temperature, from the relative duration of exposures to the high temperature, and from the losses of mass undergone by the sample. At two different temperatures, such as 850° and 900° C, it would be expected that the rates of drift of the heat value and the sample mass would be approximately proportional to the equilibrium pressures of hydrogen. This relationship was found to hold roughly, and led to the belief that the corrections applied are of at least the right order of magnitude, especially as the drifts were often decidedly outside the usual precision of measurement with this apparatus. (Presumably no problem of possibly sluggish reproportionation between two solid phases existed above 800° C.) It will be noted that this method of correction leads to exact agreement in the next-to-the-last column when only two measurements were made at the given temperature.

Alternatively, it would have been possible, in principle, to apply corrections for the losses of hydrogen calculated from a comprehensive correlation of the heat-content data with the phase diagram of the zirconium-hydrogen system. However, this was not practical for two reasons. In the first place, while it appeared that two of the samples each lost a total of 8 mg of hydrogen (most of this at 900° C), some of the loss may have been obscured by small gains of oxygen simulataneously acquired by the sample, and the two corrections are widely different per milligram change in sample mass. In the second place, the theoretical correlation would often have led to corrections that were uncertain because they involved small differences between relatively large numbers. It is interesting to note, however, that such a correlation was made and that in nearly every case the corrections so predicted had not only the same sign but also the same order of magnitude as those found empirically.

The hydride compositions were corrected for the chemical impurities by subtracting the mass of carbon, nitrogen, and oxygen and then assuming the remaining impurities to be replaced by the same number of zirconium atoms. The corresponding corrections to the heat values shown in tables 3 to 8 were made in two steps. First, the additively calculated heat contributions by the interstitial elements carbon, nitrogen, and oxygen were subtracted. Then it was assumed that the heat capacity of zirconium is the same *per atom* as that of the remaining impurities it was assumed to replace. However, in the case of carbon and silicon, appreciable deviations from equality of atomic heat capacities at the same temperature were taken into account by using the actual heat capacities of the free elements.

From the third columns of tables 3 to 8 it will be noted that in some runs the sample was first held for a while above the temperature of the measurement before being cooled for a final period of equilibration at the nominal temperature. (This elevated temperature was actually only 30 deg higher for zirconium at 870° C, and only 40 deg higher for the hydrides at 500° C.) These runs, in which equilibrium was approached from a higher temperature, were made for comparison with those approached from a lower temperature in order to set limits to the error in heat content that could have resulted from lack of phase equilibrium, and separate mean values have been recorded in the last columns of the table to show

TABLE 3. *Individual measurements of heat content—zirconium metal (sample 1)*

Furnace temperature, t	Order in which run was made	Time interval at—		Sample mass	Heat observed		Corrections for composition		Corrected $H_t-H_{0^\circ C}$, net for sample	
		$t+50°$	$t°$		With sample	Container only	Loss of H_2	Impurities	Single run	Mean (set)
°C		min	min	g	cal	cal	cal g^{-1}	cal g^{-1}	cal g^{-1}	cal g^{-1}
100	16	0	31	20.0757	288.6	150.0	0.00	0.00	6.91	6.91
	17	0	31	20.0757	288.6	150.0	.00	.00	6.91	
	24	0	39	20.0757	288.6	150.0	.00	.00	6.90	
	25	0	44	20.0757	288.6	150.0	.00	.00	6.91	
200	18	0	38	20.0757	595.3	310.6	.00	−.01	14.17	14.08
	19	0	33	20.0757	594.3	310.6	.00	−.01	14.12	
	20	0	37	20.0757	593.2	310.6	.00	−.01	14.07	
	21	0	56	20.0757	593.4	310.6	.00	−.01	14.08	
	22	0	46	20.0757	592.2	310.6	.00	−.01	14.02	
	23	0	36	20.0757	593.8	310.6	.00	−.01	14.10	
	26	0	41	20.0757	594.9	310.6	.00	−.01	14.15	
	27	0	32	20.0757	592.7	310.6	.00	−.01	14.04	
	45	0	42	20.0757	592.9	311.6	.00	−.01	14.00	
	46	0	53	20.0757	593.6	311.6	.00	−.01	14.04	
300	7	0	43	20.0757	916.5	476.7	.00	−.04	[a] (21.87)	21.80
	8	0	35	20.0757	915.1	476.7	.00	−.04	21.80	
	9	0	47	20.0757	915.4	476.7	.00	−.04	21.81	
	10	0	48	20.0757	915.0	476.7	.00	−.04	21.79	
	11	0	31	20.0757	915.0	476.7	.00	−.04	21.79	
400	12	0	31	20.0757	1240.6	648.2	.00	−.03	29.48	29.44
	13	0	31	20.0757	1240.4	648.2	.00	−.03	29.46	
	47	0	47	20.0757	1239.2	651.0	.00	−.03	29.36	
	48	0	37	20.0757	1240.8	649.2	.00	−.03	29.44	
	49	0	51	20.0757	1241.1	649.2	--------	--------	29.45	
500	3	0	30	20.0757	1574.4	825.0	.00	−.04	37.29	37.37
	4	0	30	20.0757	1578.0	825.0	.00	−.04	37.47	
	5	0	31	20.0757	1576.9	825.0	.00	−.04	37.41	
	6	0	33	20.0757	1575.7	825.0	.00	−.04	37.35	
	14	0	31	20.0757	1575.5	825.0	.00	−.04	37.34	
	15	0	34	20.0757	1575.2	825.0	.00	−.04	37.33	
600	1	0	33	20.0757	1923.6	1009.5	.00	−.06	45.47	45.46
	2	0	50	20.0757	1923.1	1009.5	.00	−.04	45.45	
700	28	0	40	20.0757	2290.0	1204.0	.00	−.08	54.02	53.97
	29	0	50	20.0757	2288.7	1204.0	.00	−.08	53.95	
	30	0	42	20.0757	2288.7	1204.0	.00	−.08	53.95	
800	31	0	61	20.0757	2666.4	1408.0	.00	−.08	62.61	62.57
	32	0	55	20.0757	2666.4	1408.0	.00	−.08	62.61	
	37	0	50	20.0757	2664.8	1408.3	.00	−.08	62.51	
	38	0	60	20.0757	2665.4	1408.3	.00	−.08	62.54	
850	33	0	60	20.0757	2863.8	1510.8	.00	−.10	67.30	67.23
	34	0	62	20.0757	2864.3	1510.8	.00	−.10	67.32	
	39	0	62	20.0757	2861.6	1511.1	.00	−.10	67.17	
	40	0	53	20.0757	2860.7	1511.1	.00	−.10	67.14	
	59	0	78	15.0776	2528.3	1513.5	.00	−.10	67.20	
	60	0	66	15.0776	2528.8	1513.5	.00	−.10	67.23	
870	43	58	52	20.0757	3123.9	1552.7	.00	−.09	78.17	78.16
	44	64	70	20.0757	3123.2	1552.7	.00	−.09	78.14	
875	54	0	60	15.0776	2760.5	1565.6	.00	−.09	79.16	79.16
880	55	0	57	15.0776	2781.5	1576.1	.00	−.09	79.86	79.86
885	50	0	63	15.0776	2801.3	1586.5	.00	−.09	80.48	80.49
	52	0	72	15.0776	2803.5	1586.5	.00	−.09	80.62	
	58	0	70	15.0776	2799.5	1586.5	.00	−.09	80.36	
890	56	0	61	15.0776	2818.3	1597.0	.00	−.09	80.91	80.91
895	57	0	57	15.0776	2835.2	1607.5	.00	−.09	81.33	81.33
900	35	0	62	20.0757	3265.1	1614.3	.00	−.09	82.14	81.91
	36	0	80	20.0757	3263.3	1614.3	.00	−.09	82.05	
	41	0	60	20.0757	3258.6	1615.4	.00	−.09	81.76	
	42	0	61	20.0757	3258.8	1615.4	.00	−.09	81.77	
	51	0	62	15.0776	2854.2	1618.0	.00	−.09	81.90	
	53	0	58	15.0776	2853.5	1618.0	.00	−.09	81.85	

[a] Omitted from the mean because of inferior precision.

these differences. It will be noted, as one would expect, that in every case the higher heat was found when the approach was from a higher temperature. Also, longer times at the nominal temperature usually narrowed the discrepancy between the two directions of approach, though not rapidly enough to be a practical means of coming as close to equilibrium as the precision of the apparatus enables one to measure.

When a hydride sample had been measured at high temperatures, such as 900° C, before being remeasured at some lower temperature in the manner described above, the remeasurements were begun in the usual way by approaching the furnace temperature from a lower temperature, and the corrections applied for previous loss of hydrogen were calculated so as to give perfect agreement with the results ob-

TABLE 4. *Individual measurements of heat content—zirconium hydride 0.356% H by weight (sample 2)*

Furnace temperature, *t*	Order in which run was made	Time interval at—		Sample mass	Heat observed		Corrections for composition		Corrected $H_t-H_{0°C}$, net for sample	
		$t+50°$	$t°$		With sample	Container only	Loss of H_2	Impurities	Single run	Mean (set)
°C		*min*	*min*	*g*	*cal*	*cal*	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$
100	13	0	67	19.8280	296.7	150.3	0.00	0.00	7.39	7.38
	14	0	43	19.8280	296.4	150.3	.00	.00	7.37	
200	15	0	42	19.8280	619.7	311.6	.00	−.02	15.52	15.50
	16	0	80	19.8280	618.9	311.6	.00	−.02	15.48	
300	6	0	63	19.8280	963.9	477.3	.00	−.04	24.50	24.49
	7	0	53	19.8280	963.5	477.3	.00	−.04	24.48	
400	4	0	64	19.8280	1337.6	650.6	.00	−.05	34.59	34.62
	5	0	50	19.8280	1338.7	650.6	.00	−.05	34.65	
500	1	0	61	19.8280	1733.1	812.6	.00	−.07	46.36	46.36
	2	0	48	19.8280	1733.2	812.6	.00	−.07	46.36	
	3	40	71	19.8280	1733.4	812.6	.00	−.07	46.37	46.37
540	23	0	69	19.1375	1881.0	899.8	+.15	−.08	51.34	51.38
	24	0	52	19.1375	1882.2	899.8	−.15	−.08	51.41	
550	8	0	64	19.8280	2062.1	918.0	−.15	−.08	57.62	57.86
	9	0	49	19.8280	2032.2	918.0	−.15	−.08	[a](56.11)	
	22	0	78	19.1375	2028.8	918.0	+.15	−.08	58.11	
600	10	0	52	19.8280	2561.8	1010.5	+.15	−.08	78.16	78.14
	11	0	72	19.8280	2560.9	1010.5	+.15	−.08	78.11	
	12	40	74	19.8280	2565.3	1010.5	+.15	−.08	78.33	78.37
	17	40	96	19.8280	2566.8	1010.5	+.15	−.08	78.41	
700	18	40	56	19.8280	2741.6	970.1	.00	−.11	89.24	89.24
	19	0	87	19.8280	2741.1	970.1	.00	−.11	89.21	89.21
800	20	0	70	19.8280	3083.1	1132.9	+.12	−.12	98.36	98.31
	21	0	57	19.8280	3079.3	1132.9	+.22	−.12	98.26	
900	25	0	61	19.1375	3675.6	1615.4	+.35	−.13	107.87	107.76
	26	0	76	19.1375	3668.9	1615.4	+.48	−.13	107.65	

[a] Given no weight. Apparently the time in the furnace was inadequate.

tained before the exposure to higher temperatures. This method of applying corrections for previous loss of hydrogen did not, of course, affect the principal purpose of making a new series of measurements, which was to ascertain the difference in heat resulting from heating and from cooling the sample to the desired furnace temperature.

4. Mean Heat Capacities of Zirconium and the Zirconium Hydride Samples

The heat content of zirconium has been measured by Mixter and Dana (0° to 100° C) [3], Jaeger and Veenstra (21° to 801° C) [4], Coughlin and King (25° to 1,098° C) [5], Skinner (25° to 1,000° C) [6], Redmond and Lones (150° to 1,050° C) [7], and Scott (60° to 960° C) [8]. Reviewing the first two investigations, Kelley [9] gave equations for the heat content and heat capacity over the range 25° to 627° C. Scott's zirconium had a purity comparable to that indicated in table 2, but presumably most of the earlier measurements were on samples containing considerable hafnium for which no corrections were applied. According to Dulong and Petit's law, in the case of zirconium each 1 percent of hafnium would lower the observed heat content and heat capacity per unit mass by about ½ percent.

Pure zirconium metal undergoes a transformation of crystalline structure at a temperature that, partly due to its sensitivity to small amounts of certain impurities, does not seem to be known very precisely. Coughlin and King [5] observed a rapid rise in heat content over a range of some 80 deg C. Since it is known that oxygen or nitrogen, when dissolved in the metal, has such an effect, they assumed their sample to contain one or both of these impurities. The heat-content measurements of Redmond and Lones [7] were of low precision, and they reported no evidence for a heat-absorbing transformation. Though two investigators [6, 8] reported 870° C as the transformation temperature, two compilations [10, 11] have given 862° and 863° C, respectively, and the last temperature has been somewhat arbitrarily assumed in this paper. (The assumption of another of these temperatures would have had very little effect on the value of the heat of transformation derived from the data.)

The present authors were limited by their apparatus to temperatures not higher than 40 deg C above the transformation temperature. As the preliminary measurements at 870° and 900° C had indicated a value for the mean heat capacity between these two temperatures of 11 cal/g atom-deg C, a value that seems too high for this element, additional measurements of heat content were made at 5-deg intervals over this temperature range. The mean relative heat content at each of these temperatures (last column of table 3) is plotted in figure 1. Considering the very small temperature intervals and the large magnitudes of all these measured heats, the precision is good; but (above the transformation temperature) there is a decided negative curvature at the lower temperatures, which may be due to small amounts of oxygen and nitrogen.

Table 5. *Individual measurements of heat content—zirconium hydride, 0.611% H by weight (sample 3)*

Furnace temper-ature, t	Order in which run was made	Time interval at—		Sample mass	Heat observed		Corrections for composition		Corrected $H_t-H_{0°C}$, net for sample	
		t+50°	t°		With sample	Container only	Loss of H_2	Impurities	Single run	Mean (set)
°*C*		*min*	*min*	*g*	*cal*	*cal*	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$
100	1	0	54	19.6516	291.6	150.4	0.00	−0.16	[a](7.02)	
	2	0	40	19.6516	303.5	150.4	.00	−.16	7.63	7.62
	3	0	42	19.6516	303.7	150.4	.00	−.16	7.64	
	4	0	52	19.6516	303.0	150.4	.00	−.16	7.60	
200	5	0	54	19.6516	640.2	310.3	.00	−.36	16.42	16.42
	6	0	37	19.6516	640.1	310.3	.00	−.36	16.42	
300	7	0	47	19.6516	1011.4	475.3	.00	−.58	26.70	26.70
	8	0	41	19.6516	1011.2	475.3	.00	−.58	26.69	
400	9	0	42	19.6515	1402.7	648.0	.00	−.85	37.55	
	10	0	38	19.6516	1403.0	648.0	.00	−.85	37.57	
	13	0	51	19.6516	1402.5	648.0	.00	−.85	37.55	
	19	0	40	19.6516	1404.4	648.0	.00	−.85	37.64	
	20	0	51	19.6516	1404.3	648.0	.00	−.85	37.64	37.57
	25	0	55	19.6516	1402.7	648.0	.00	−.85	37.56	
	26	0	40	19.6516	1402.6	648.0	.00	−.85	37.55	
	27	0	56	19.6516	1402.0	648.0	.00	−.85	37.52	
	28	0	41	19.6516	1402.9	648.0	.00	−.85	37.57	
500	11	0	54	19.6516	1831.5	826.3	.00	−1.12	50.03	
	12	0	40	19.6516	1830.6	826.3	.00	−1.12	49.98	50.00
	40	0	52	18.8850	1789.6	827.0	+.09	−1.12	49.94	
	41	0	71	18.8850	1791.7	827.0	+.09	−1.12	50.06	
	42	41	55	18.8850	1791.1	827.0	+.09	−1.12	50.03	50.02
	43	38	43	18.8850	1790.7	827.0	+.09	−1.12	50.00	
550	16	0	50	19.6516	2063.6	916.8	.00	−1.29	57.07	
	17	0	76	19.6516	2062.2	916.8	.00	−1.29	57.00	57.02
	18	0	40	19.6516	2061.8	916.8	.00	−1.29	56.98	
575	29	0	45	19.6516	2386.1	962.9	.00	−1.52	70.90	
	30	0	76	19.6516	2404.8	962.9	.00	−1.52	71.85	70.1
	33	0	110	19.6516	2318.4	962.9	.00	−1.52	67.46	
600	14	0	41	19.6516	2663.2	1009.8	.00	−1.72	82.42	
	15	0	80	19.6516	2660.7	1009.8	.00	−1.72	82.29	82.36
	36	0	40	18.8850	2578.4	1010.5	+1.05	−1.72	82.35	
	37	0	80	18.8850	2578.8	1010.5	+1.05	−1.72	82.37	
	38	41	40	18.8850	2642.1	1010.5	+1.05	−1.72	85.72	85.67
	39	40	78	18.8850	2640.1	1010.5	+1.05	−1.72	85.62	
650	31	0	40	19.6516	2953.6	1106.8	0.00	−1.90	92.08	
	32	0	52	19.6516	2955.0	1106.8	.00	−1.90	92.15	92.12
	44	0	40	18.8850	2870.4	1115.7	+1.11	−1.90	92.12	
	45	0	61	18.8850	2870.6	1115.7	+1.11	−1.90	92.14	
	46	40	60	18.8850	2871.6	1115.7	+1.11	−1.90	92.19	92.24
	47	40	93	18.8850	2873.4	1115.7	+1.11	−1.90	92.28	
700	21	0	54	19.6516	3174.3	1205.6	0.00	−2.05	98.13	98.15
	22	0	40	19.6516	3175.1	1205.6	.00	−2.05	98.17	
800	23	0	40	19.6516	3624.9	1409.1	+.07	−2.34	110.48	110.48
	24	0	50	19.6516	3623.1	1409.1	+.16	−2.34	110.48	
900	34	0	40	19.6516	4059.9	1616.1	+.38	−2.61	122.13	122.13
	35	0	55	19.6516	4053.8	1616.1	+.69	−2.61	122.13	

[a] Omitted from the mean because of inferior precision.

The straight line was drawn on the assumption that the scatter of points at and above 880° C is random. The mean heat capacity of β-zirconium corresponding to the slope of this line is subject to considerable uncertainty because of the smallness of the total temperature interval. Extrapolation to the transformation temperature leads to a value of 9.8 cal g^{-1} for the heat of transformation of the metal. The following values (in the same units) have previously been given: 4.7 [12], 7.7 [10], 10.1 [5], 10.9 [8], and 11.4 [6]. The large spread of these values is undoubtedly largely due to the usual necessity of interpolating the heat content of this element through a considerable temperature range because the transformation indicated by the thermal data was not sharp.

In table 9 are given the values of mean heat capacity of zirconium observed in the present investigation. These values were calculated from the differences between successive values in the last column of table 3 up to 850° C, and from the line in figure 1 above 863° C. Also given for comparison are the percentage deviations of the smoothed values of other investigators from the values of the second column.

Similarly, the mean observed heat capacities of the five samples of zirconium hydride whose heat contents were measured were calculated for the temperature intervals of measurement from the successive differences in the last columns of tables 4 to 8. These values are given in table 10. (The compositions may be identified from table 1.) In the intervals where the apparent heat capacity was found to be unusually large, particularly between 550° and 600° C, extensive phase transformation was occurring, and as a consequence the effective

Table 6. *Individual measurements of heat content—zirconium hydride, 0.769% H by weight (sample 4)*

Furnace temperature, t	Order in which run was made	Time interval at—		Sample mass	Heat observed		Corrections for composition		Corrected $H_t-H_{0°C}$, net for sample	
		t+50°	t°		With sample	Container only	Loss of H_2	Impurities	Single run	Mean (set)
°C		*min*	*min*	*g*	*cal*	*cal*	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$
100	1	0	56	19.3007	303.2	150.4	0.00	−0.12	7.79	7.80
	2	0	39	19.3007	303.2	150.4	.00	−.12	7.80	
200	3	0	55	19.3007	642.6	310.3	.00	−.29	16.92	16.93
	4	0	40	19.3007	642.8	310.3	.00	−.29	16.94	
300	5	0	56	19.3007	1019.8	475.3	.00	−.48	27.73	27.71
	6	0	41	19.3007	1019.0	475.3	.00	−.48	27.69	
400	7	0	58	19.3007	1414.1	648.0	.00	−.71	38.98	38.97
	8	0	40	19.3007	1413.6	648.0	.00	−.71	38.96	
500	9	0	56	19.3007	1847.4	826.3	.00	−.92	51.98	51.99
	10	0	41	19.3007	1847.7	826.3	.00	−.92	52.00	
	30	0	60	19.3007	1847.6	826.3	+.05	−.92	52.05	
	31	0	57	19.3007	1845.8	826.3	+.05	−.92	51.95	
	32	0	60	19.3007	1845.8	826.3	+.05	−.92	51.95	
	33	0	60	19.3007	1846.7	826.3	+.05	−.92	52.00	
550	13	0	56	19.3007	2085.9	917.4	.00	−1.06	59.48	59.54
	14	0	187	19.3007	2091.1	917.4	.00	−1.06	59.75	
	15	0	52	19.3007	2084.2	917.4	.00	−1.06	59.39	
560	20	0	56	19.3007	2217.4	935.9	.00	−1.11	65.29	64.5
	21	0	126	19.3007	2199.5	935.9	.00	−1.11	64.36	
	22	0	62	19.3007	2189.6	935.9	.00	−1.11	63.85	
575	18	0	53	19.3007	2508.5	963.7	.00	−1.28	78.76	78.67
	19	0	89	19.3007	2505.1	963.7	.00	−1.28	78.58	
600	11	0	56	19.3007	2722.3	1009.8	.00	−1.40	87.33	87.37
	12	0	89	19.3007	2723.9	1009.8	.00	−1.40	87.41	
	35	0	42	16.7834	2507.0	1021.7	+.17	−1.40	87.27	
	36	0	73	16.7834	2510.6	1021.7	+.17	−1.40	87.48	
	37	40	61	16.7834	2535.8	1021.7	+.17	−1.40	88.99	88.88
	38	40	95	16.7834	2532.4	1021.7	+.17	−1.40	88.78	
650	16	0	51	19.3007	3037.2	1107.0	.00	−1.55	98.46	98.41
	17	0	40	19.3007	3035.2	1107.0	.00	−1.55	98.35	
	39	0	43	16.7834	2779.5	1115.7	+.83	−1.55	98.42	
	40	0	60	16.7834	2779.2	1115.7	+.83	−1.55	98.40	
	41	41	66	16.7834	2778.9	1115.7	+.83	−1.55	98.38	98.42
	42	41	90	16.7834	2780.2	1115.7	+.83	−1.55	98.45	
700	23	0	50	19.3007	3252.5	1205.6	.00	−1.67	104.38	104.36
	24	0	41	19.3007	3251.6	1205.6	.00	−1.67	104.34	
800	25	0	45	19.3007	3691.4	1409.1	+.07	−1.90	116.42	116.39
	26	0	42	19.3007	3688.2	1409.1	+.14	−1.90	116.32	
	27	0	45	19.3007	3689.1	1409.1	+.21	−1.90	116.44	
900	28	0	55	19.3007	4127.6	1616.1	+.48	−2.12	128.48	128.48
	29	0	40	19.3007	4124.1	1616.1	+.68	−2.12	128.50	
	34	0	50	19.3007	4118.6	1616.1	+.93	−2.12	128.47	

heat capacity was not only changing rapidly with temperature but the mean values recorded are subject to large uncertainties because of the impossibility of reaching equilibrium in the measurements within a reasonable time. On the other hand, in those temperature ranges where mean heat capacity appears to vary regularly with temperature (particularly from 0° to 540° or 550° C), it is justifiable to assume the recorded values to be the instantaneous heat capacities in the middle of their respective temperature ranges and to interpolate for intermediate temperatures in the usual way.

The regions of regular variation can be more quickly located by an inspection of figure 2, since for each composition, each two adjacent points are connected by a straight line whose slope is proportional to the corresponding value in table 10. It is also justifiable to interpolate for values for intermediate compositions at any temperature up to 540° C, as discussed in section 5.

5. Discussion of the Heat Capacities of the Hydride Samples

The observed discontinuities in the heat-capacity-temperature functions of the five samples of zirconium hydride can be interpreted qualitatively in terms of the phase diagram of the system. One version of this diagram is shown in figure 3. The three solid solutions indicated are designated α, β, and γ. A similar diagram was given by Vaughan and Bridge as a result of their high-temperature X-ray diffraction studies [13]; but the results of different investigators, using various methods, do not agree well as to the shapes of some of the phase-field boundaries, two of which seem to be particularly uncertain and are therefore shown as dashed lines. The dotted vertical lines and their points indicate the compositions and temperatures for which measured values of relative heat content are reported in this paper.

TABLE 7. *Individual measurements of heat content—zirconium hydride, 1.029%* H *by weight (sample 5)*

Furnace temper-ature, t	Order in which run was made	Time interval at—		Sample mass	Heat observed		Corrections for com-position		Corrected $H_t-H_{0°C}$, net for sample	
		t+50°	t°		With sample	Container only	Loss of H_2	Impurities	Single run	Mean (set)
°*C*		*min*	*min*	*g*	*cal*	*cal*	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$	*cal g*$^{-1}$
100	1	0	51	18.9319	306.5	150.0	0.00	−0.12	8.15	8.15
	2	0	44	18.9319	306.5	150.0	.00	−.12	8.15	
200	3	0	40	18.9319	655.7	310.6	.00	−.30	17.93	18.00
	4	0	41	18.9319	656.3	310.6	.00	−.30	17.96	
	5	0	41	18.9319	657.5	310.6	.00	−.30	18.02	
	14	0	42	18.9319	679.4	310.6	.00	−.30	[a](19.18)	
	15	0	58	18.9319	658.0	310.6	.00	−.30	18.05	
	16	0	43	18.9319	658.0	310.6	.00	−.30	18.05	
300	6	0	38	18.9319	1050.1	476.7	.00	−.49	29.80	29.69
	7	0	41	18.9319	1048.7	476.7	.00	−.49	29.72	
	8	0	45	18.9319	1048.4	476.7	.00	−.49	29.71	
	17	0	46	18.9319	1046.3	476.4	.00	−.49	29.60	
	18	0	54	18.9319	1045.8	476.4	.00	−.49	29.57	
	19	0	42	18.9319	1049.0	476.4	.00	−.49	29.74	
400	11	0	60	18.9319	1462.4	648.2	.00	−.73	42.27	42.30
	12	0	48	18.9319	1461.3	648.2	.00	−.73	42.22	
	13	0	53	18.9319	1461.2	648.2	.00	−.73	42.21	
	33	0	46	18.9319	1464.1	648.2	.00	−.73	42.37	
	34	0	60	18.9319	1464.9	648.2	.00	−.73	42.41	
	41	0	48	18.9319	1456.0	648.2	+.38	−.73	42.32	
	42	0	61	18.9319	1455.7	648.2	+.38	−.73	42.30	
500	9	0	57	18.9319	1910.4	825.0	.00	−.97	56.36	56.39
	10	0	43	18.9319	1911.7	825.0	.00	−.97	56.43	
	43	0	50	17.2397	1796.3	812.6	+.30	−.97	56.39	
	44	0	70	17.2397	1796.3	812.6	+.30	−.97	56.39	
	45	40	52	17.2397	1798.7	812.6	+.30	−.97	56.53	56.59
	46	30	80	17.2397	1800.8	812.6	+.30	−.97	56.65	
550	20	0	53	18.9319	2164.4	917.2	.00	−1.11	64.77	64.56
	21	0	41	18.9319	2160.3	917.2	.00	−1.11	64.56	
	22	0	62	18.9319	2158.4	917.2	.00	−1.11	64.45	
	23	0	75	18.9319	2158.4	917.2	.00	−1.11	64.45	
575	26	0	60	18.9319	2384.2	963.4	.00	−1.23	73.82	73.62
	27	0	64	18.9319	2376.8	963.4	.00	−1.23	73.43	
600	24	0	62	18.9319	2561.3	1009.5	.00	−1.33	80.64	80.67
	25	0	70	18.9319	2562.6	1009.5	.00	−1.33	80.71	
	47	0	51	17.2397	2408.0	992.9	−.10	−1.33	80.66	
	48	0	72	17.2397	2408.3	992.9	−.10	−1.33	80.67	
	49	40	52	17.2397	2416.0	992.9	−.10	−1.33	81.12	81.10
	50	40	79	17.2397	2415.5	992.9	−.10	−1.33	81.09	
650	28	0	60	18.9319	2878.4	1107.9	.00	−1.49	92.03	92.02
	29	0	53	18.9319	2877.8	1107.9	.00	−1.49	92.00	
700	30	0	54	18.9319	3179.5	1204.0	.00	−1.67	102.68	102.77
	31	0	60	18.9319	3182.4	1204.0	.00	−1.67	102.83	
	32	0	75	18.9319	3181.9	1204.0	.00	−1.67	102.81	
	51	0	53	17.2397	2991.6	1182.9	−.54	−1.67	102.70	
	52	0	72	17.2260	2992.3	1182.9	−.54	−1.67	102.83	
	53	43	67	17.2260	3011.1	1182.9	−.54	−1.67	[b](103.92)	103.02
	54	43	91	17.2260	2995.7	1182.9	−.54	−1.67	103.02	
750	35	0	60	18.9319	3478.7	1305.3	.00	−1.82	112.98	113.01
	36	0	63	18.9319	3479.8	1305.3	.00	−1.82	113.04	
800	37	0	60	18.9319	3786.4	1408.0	.00	−1.97	123.66	123.76
	38	0	85	18.9319	3790.3	1408.0	.00	−1.97	123.87	
850	39	0	61	18.9319	4086.2	1510.8	+.40	−2.14	134.30	134.32
	40	0	60	18.9319	4086.9	1510.8	+.40	−2.14	134.34	
	55	0	57	17.2260	3836.5	1510.8	+1.45	−2.14	134.32	
	56	0	61	17.2260	3830.5	1510.8	+1.80	−2.14	134.32	
900	57	0	61	17.2260	4044.3	1615.4	+2.26	−2.25	141.01	141.01
	58	0	58	17.2260	4028.4	1615.4	+3.18	−2.25	141.01	

[a] Omitted from mean because of inferior precision. [b] Given no weight. Apparently the time in the furnace was inadequate.

The mean observed heat contents up to 500° C of zirconium and the five hydride samples, taken from the last columns of tables 3 to 8 and converted to cal mole^{-1} of ZrH_x, are plotted against the over-all composition x in figure 4. The linearity of the values for the five hydride samples is in general good and accords with the prediction of the phase diagram (fig. 3) that these five samples are mixtures in different proportions of the same two phases at each temperature up to 550° C. (The sample $ZrH_{0.234}$ obeys this relation only up to 540° C.) In fact, the proximity of the observed points to the fairly steep lines at the higher temperatures may be considered to afford an approximate check on the general interconsistency of the hydride compositions found by analysis. The coefficients of the equations of the straight lines drawn through these points in figure 4 were determined by the method of least squares and

TABLE 8. *Individual measurements of heat content—zirconium hydride, 1.170% H by weight (sample 6)*

Furnace temperature, t	Order in which run was made	Time interval at—		Sample mass	Heat observed		Corrections for composition		Corrected $H_t-H_{0^\circ C}$, net for sample	
		$t+50^\circ$	t°		With sample	Container only	Loss of H_2	Impurities	Single run	Mean (set)
°C		*min*	*min*	*g*	*cal*	*cal*	*cal g⁻¹*	*cal g⁻¹*	*cal g⁻¹*	*cal g⁻¹*
100	10	0	58	18.6311	276.1	122.9	0.00	−0.01	8.21	8.23
	11	0	66	18.6311	276.8	122.9	.00	−.01	8.25	
200	12	0	65	18.6311	593.3	251.9	.00	−.03	18.29	18.29
300	7	0	55	18.6311	944.8	385.8	.00	−.04	30.10	29.99
	8	0	84	18.6311	943.2	385.8	.00	−.04	29.88	
400	9	0	57	18.6311	1321.0	524.2	.00	−.05	42.72	42.72
500	1	0	73	18.6311	1735.2	666.6	.00	−.08	57.27	57.27
	2	45	93	18.6311	1739.2	666.6	.00	−.08	57.49	57.49
550	3	0	66	18.6311	1981.6	740.5	.00	−.08	66.53	66.42
	4	0	57	18.6311	1977.4	740.5	.00	−.08	66.31	
600	5	0	73	18.6311	2451.0	815.2	.00	−.09	87.71	87.71
	6	40	72	18.6311	2458.0	815.2	.00	−.09	88.08	88.08
700	13	0	80	16.6219	3044.8	1207.6	.00	−.11	110.43	110.42
	14	0	61	16.6219	3044.2	1207.6	.00	−.11	110.40	
800	15	0	60	16.6219	3587.8	1410.7	.00	−.13	130.86	130.92
	16	0	50	16.6219	3589.8	1410.7	.00	−.13	130.98	
850	17	0	52	16.6219	3799.5	1513.5	+.17	−.14	137.57	137.57
	18	0	64	16.6219	3795.5	1513.5	+.41	−.14	137.57	
900	19	0	50	16.6219	3996.2	1618.0	+1.11	−.15	144.05	144.05
	20	0	60	16.6219	3972.8	1618.0	+2.52	−.15	144.05	

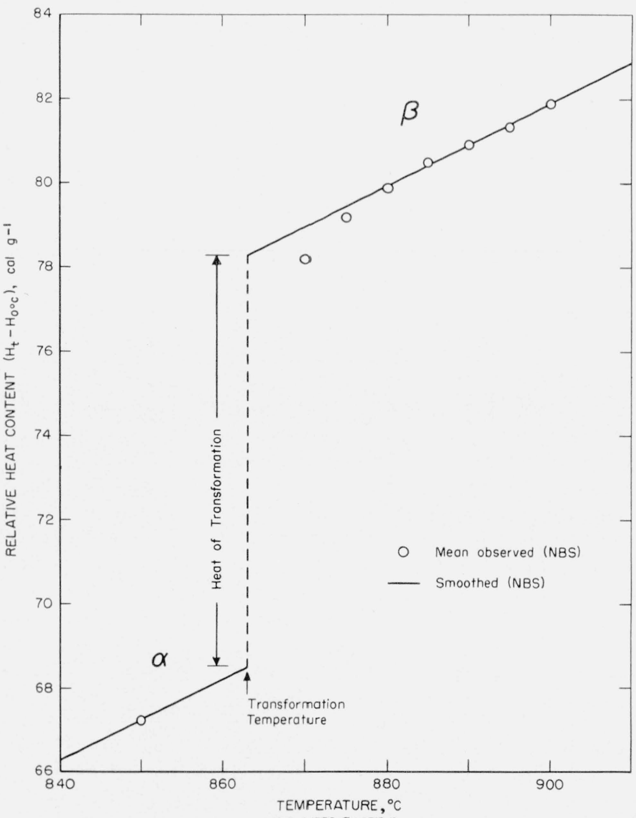

FIGURE 1. *Heat content of zirconium near its transformation temperature.*

are given in table 11. These relations can be used as a means of interpolating below 550° C for smooth values of the relative heat contents of compositions on which no measurements were made.

The phase diagram shown in figure 3 indicates a first-order phase transition at a eutectoid temperature of approximately 550° C. Though the slopes in figure 2 represent only average heat capacities over the finite temperature intervals of measurement, it is apparent that the heat capacity of each hydride sample reaches a maximum value within the range 540° to 600° C, corresponding to this phase transition. However, it will be observed that the particularly high heat capacities are spread over a temperature range, a fact to be interpreted as due to considerable lack of phase equilibrium at these temperatures. This is not an unusual situation in the case of all-solid systems. The interpretation is supported by the unusually poor reproducibility of duplicate heat values at 560° and 575° C and the hysteresis found at 600° C, as may be noted from the last two columns of tables 4 to 8.

As the temperature rises above 600° C, the heat capacities of samples 3 to 6 decrease rather abruptly to smaller values at temperatures that differ for the four samples. This fact also can be given a qualitative interpretation in terms of the phase diagram, for above a certain temperature each hydride sample investigated should become all β phase, and therefore at higher temperatures there would no longer be a contribution to the over-all, or observed, heat capacity by latent heat of phase reproportionation.

Table 9. *Mean observed heat capacities of zirconium metal*

Temperature interval	Mean heat capacity (this investigation)	Deviations of smoothed values of other investigators				
		Bulletin 476 [9]	Coughlin and King [5]	Skinner [6]	Redmond and Lones [7]	Scott [8]
°C	*cal* g^{-1} *deg* C^{-1}	%	%	%	%	%
0 to 100	0.0691	−2	+1	−3	+2	−2
100 to 200	.0717	−3	+4	−2	+5	−3
200 to 300	.0772	−6	+1	−5	+2	−8
300 to 400	.0764	0	+5	0	+8	−6
400 to 500	.0793	+2	+3	−1	+9	−7
500 to 600	.0809	+5	+3	0	+11	−7
600 to 700	.0851	-----	0	−2	+10	−9
700 to 800	.0860	-----	+1	0	+13	−7
800 to 850	.0932	-----	−6	−6	+7	−11
850 to 863	.099	-----	−11	−10	+2	−15
Heat of transformation (cal g^{-1})	9.8	-----	+3	+17	-----	+11
863 to 900	0.097	-----	−18	−24	-----	−26

Table 10. *Mean observed heat capacities of five samples of zirconium hydride*

Temperature range	Sample 2 (x=0.324)	Sample 3 (x=0.556)	Sample 4 (x=0.701)	Sample 5 (x=0.999)	Sample 6 (x=1.071)
°*C*	*cal* g^{-1} *deg* C^{-1}	*cal* g^{-1} *deg* C^{-1}	*cal* g^{-1} *deg* C^{-1}	*cal* g^{-1} *deg* C^{-1}	*cal* g^{-1} *deg* C^{-1}
0 to 100	0.0738	0.0762	0.0780	0.0815	0.0823
100 to 200	.0812	.0880	.0913	.0985	.1006
200 to 300	.0899	.1028	.1078	.1169	.1170
300 to 400	.1013	.1087	.1126	.1261	.1273
400 to 500	.1174	.1244	.1302	.1419	.1466
500 to 540	.1255	.1402 (500 to 550)	.1510 (500 to 550)	.1614 (500 to 550)	.1808 (500 to 550)
540 to 550	.648				
550 to 560	.408 (550 to 600)	.522 (550 to 575)	.50	.362 (550 to 575)	.430 (550 to 600)
560 to 575			.945		
575 to 600		.56	.378	.290	
600 to 650	.1096 (600 to 700)	.163	.206	.2228	.2252 (600 to 700)
650 to 700		.1194	.1188	.2176	
700 to 750	.0909 (700 to 800)	.1233 (700 to 800)	.1203 (700 to 800)	.2022	.2050 (700 to 800)
750 to 800				.2150	
800 to 850	.0945 (800 to 900)	.1165 (800 to 900)	.121 (800 to 900)	.2112	.1330
850 to 900				.134	.130

Table 11. *Equations of smoothed heat content versus composition of zirconium hydrides up to 550°C*

$H_t - H_{0°C} = A + Bx$, cal per mole of ZrH_x		
Temperature, t	***A***	***B***
°*C*		
100	637.5	114.0
200	1305.6	356.5
300	2041.8	694.9
400	2849.4	1039.7
500	3794.2	1410.0
550	4277.0	1705.8

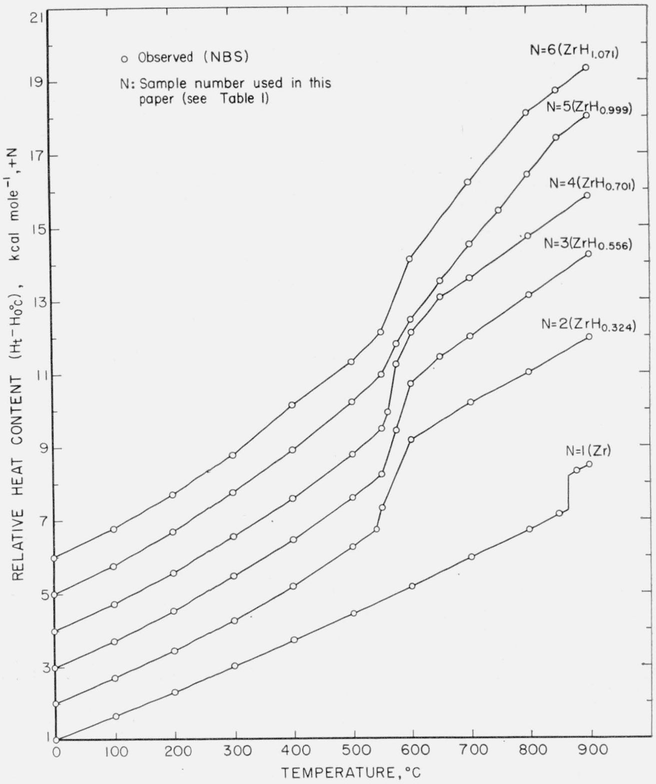

Figure 2. *Heat content versus temperature, zirconium and several zirconium hydrides.*

With due consideration to those few cases where phase equilibrium was obviously not reached during the measurements of heat content, it is possible to derive numerous quantitative energy and phase relations in the zirconium-hydrogen system from the precise thermal data reported in this paper. Such derivations are described in detail in a current publication [2].

The zirconium metal and its analysis were received from the U. S. Department of the Interior, Bureau of Mines, Albany, Oregon, through the courtesy of M. L. Wright. Several members of the National Bureau of Standards staff performed valuable services during the work. J. K. Russell made a number of the heat-content measurements on two of the hydride samples. Martha Darr carried out all the spectrochemical analyses of the Sylvania hydride samples, and R. A. Paulson analyzed the zirconium metal and duplicates of the Sylvania hydride samples for carbon and hydrogen.

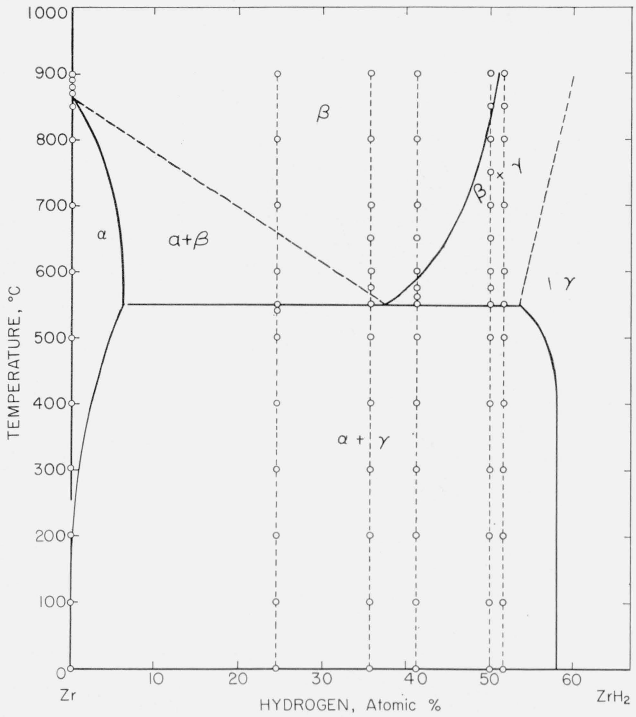

FIGURE 3. *Phase diagram of the* Zr-H *system.*

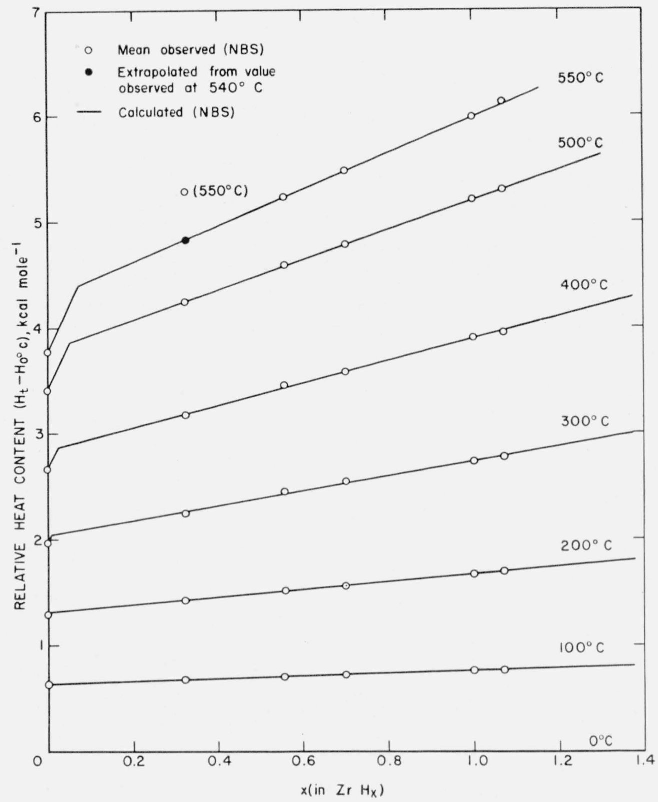

FIGURE 4. *Heat content versus composition of the* Zr-H *system,* 0° *to* 550° *C.*

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