NAA-SR-5015
CHEMISTRY-GENERAL
26 PAGES

THE ZIRCONIUM-HYDROGEN SYSTEM AT HIGH HYDROGEN CONTENTS

By
G. G. LIBOWITZ

ATOMICS INTERNATIONAL

A DIVISION OF NORTH AMERICAN AVIATION, INC.
P.O. BOX 309 CANOGA PARK, CALIFORNIA

CONTRACT: AT(11-1)-GEN-8
ISSUED: JUN 30 1960

DISTRIBUTION

This report has been distributed according to the category "Chemistry — General" as given in "Standard Distribution Lists for Unclassified Scientific and Technical Reports" TID-4500 (15th Ed.), August 1, 1959. A total of 600 copies was printed.

CONTENTS

TABLES

FIGURES

CONTENTS

Page

ABSTRACT

In order to elucidate the phase diagram of the zirconium-hydrogen system at high hydrogen contents, a pressure-composition-temperature study of this system in the temperature range 550 to 850°C has been carried out from ZrH to ZrH_2. From the isotherms obtained in this investigation, the position of the boundary between the two-phase ($\beta + \delta$) region and the single phase δ region was more precisely defined (where β designates the hydrogen stabilized high temperature zirconium phase, and δ the cubic hydride phase). The isotherms also show no evidence of a two-phase hydride region (cubic + tetragonal hydrides coexisting) in this temperature range, as has been observed at room temperature.

I. INTRODUCTION

Several recent studies[1-7] of the zirconium-hydrogen system have led to the phase diagram shown in Figure 1. Except for the X-ray study[5], the agreement between the different investigations is good at lower hydrogen contents. The α and β phases are, respectively, the low and high temperature modifications of zirconium metal containing dissolved hydrogen. A cubic hydride phase, which has usually been designated as the δ-phase, is also formed.

At higher hydrogen contents, however, the system is not as well defined. As can be seen in Figure 1, there is very poor agreement as to the position of the boundary between the two-phase ($\beta + \delta$) region and the single-phase hydride region. In addition, there is some question as to whether the ϵ-phase in Figure 1, which has a tetragonal structure, is actually a separate hydride, or whether it arises from continuous anisotropic expansion of the cubic δ-phase as reported by Vaughan and Bridge.[5] Several investigators[8-10] have observed a two-phase ($\delta + \epsilon$) region by X-rays.

The purpose of the present investigation was (1) to establish, with greater accuracy, the position of the boundary between the ($\beta + \delta$) region and the single phase δ-region from pressure-composition isotherms, (2) to determine if a two-phase ($\delta + \epsilon$) region exists at elevated temperatures, and (3) to obtain accurate and precise pressure-composition-temperature data for comparison with P-C-T expressions to be derived from theoretical considerations.

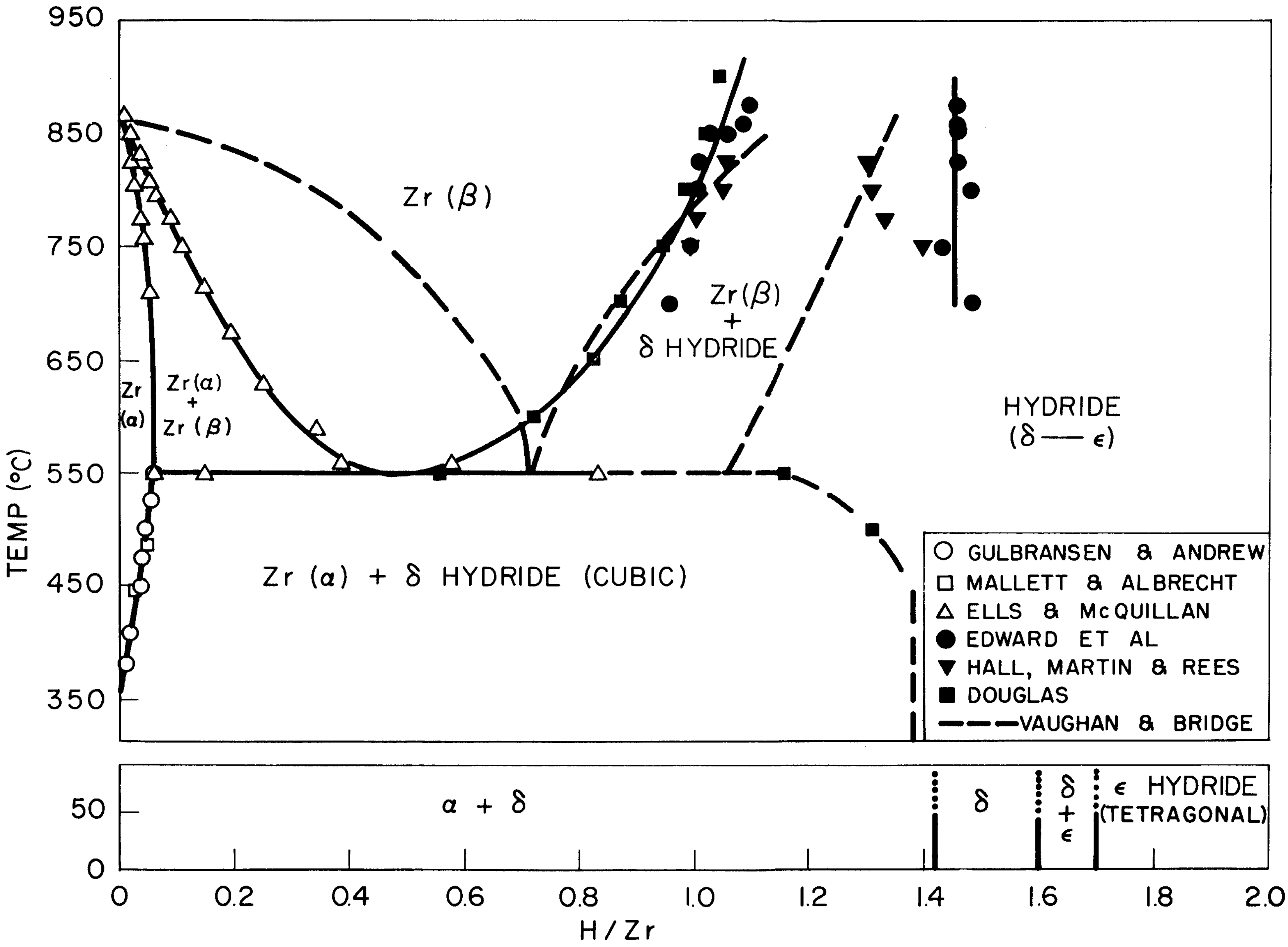

Figure 1. The Zirconium-Hydrogen Phase Diagram Before Present Investigation

II. EXPERIMENTAL

A. MATERIALS

The metal used was hafnium-free crystal bar zirconium. Spectroscopic analysis of the metal revealed the following impurities: Fe 0.03%, Ti 0.02%, and Si 0.03%; a vacuum fusion analysis showed that, originally, 0.003% oxygen and .004% hydrogen was present. Before placing it into the apparatus, the 15 to 20 gm ingot of zirconium was cleaned with an etching solution consisting of water, nitric acid, and hydrofluoric acid in the ratios 10:9:1, respectively. Four separate zirconium samples were used during the course of this investigation.

The hydrogen gas was obtained from the decomposition of uranium hydride.

B. APPARATUS

The gas-handling apparatus used in this investigation is shown in Figure 2. The zirconium sample was contained in a stainless steel or molybdenum crucible which, in turn, was contained in a quartz sample tube. The sample tube, connected to the manifold through a standard taper water-cooled glass joint, was placed in a Marshall resistance furnace. The sample was kept within a zone of constant temperature. The temperature was kept constant to within ±0.5°C by a West Temperature Controller and measured by means of a Leeds and Northrup Potentiometer and chromel-alumel thermocouple which was inserted into a well at the bottom of the sample tube.

Between 25 and 800 mm of mercury, the hydrogen pressure was measured with a mercury manometer. Below 25 mm, a 3-scale McLeod gauge (0 to 25 mm, 0 to 5 mm, 0 to 0.5 mm) was used to measure pressure.

For the removal and addition of measured amounts of hydrogen, two calibrated bulbs (200 cc and 2000 cc) were added to the apparatus. In addition, the volume of each portion of the apparatus was calibrated. The volume in the manometer, as a function of the height of the mercury, was calculated from the diameter of the glass tubing.

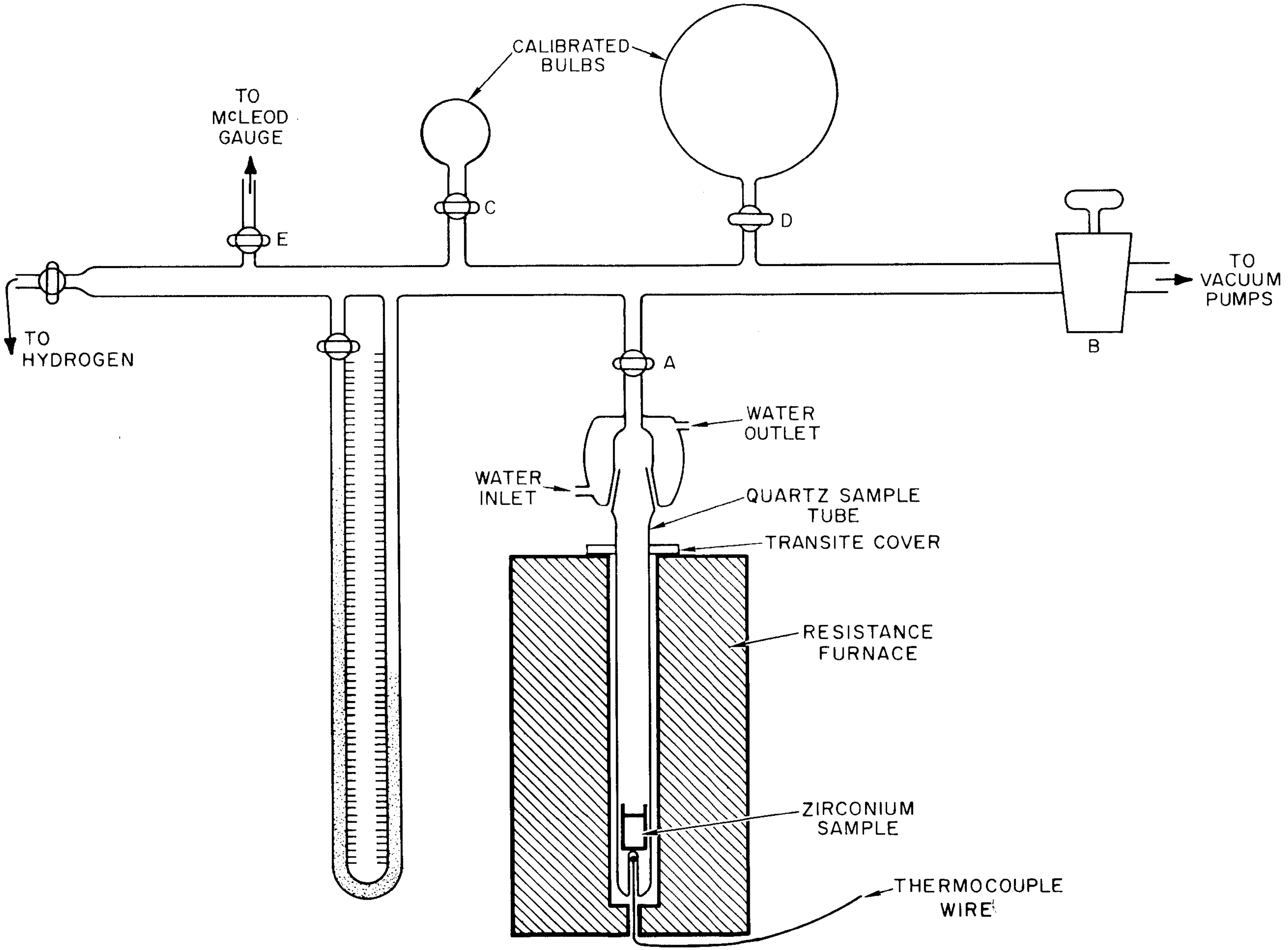

Figure 2. Apparatus for Determining Pressure-Composition Isotherms of Hydrides

C. EXPERIMENTAL PROCEDURE

The zirconium metal was completely hydrided by adding measured amounts of hydrogen gas at about 550°C and cooling to room temperature in the presence of excess hydrogen. The hydride was then heated to the temperature at which an isotherm was to be determined, and the pressure of hydrogen was measured after it had remained constant for at least two hours. The composition of the sample was calculated by subtracting the amount of gas in the system from the original amount of hydrogen in the sample. Stopcock A was then closed and a measured volume of gas withdrawn from the manifold through stopcock B. By opening stopcocks C and/or D before closing stopcock A, varying amounts of gas could be removed from the sample to bring it to any desired composition. After withdrawing the hydrogen, stopcock B was closed, stopcock A opened, and the system allowed to come to equilibrium. The pressure was then measured on the manometer, and the new composition was calculated by subtracting the gas removed plus the gas in the system above the sample from the total amount of hydrogen originally present in the sample. This procedure was repeated until a run was completed. When the pressure reached a value below 25 mm, stopcock E was opened and the pressure measured on the McLeod gauge for greater accuracy. At least three runs were made at each temperature. After each run, the hydrogen content was brought back to the maximum value by re-hydriding.

In calculating the composition during a run, the fact that a portion of the hydrogen in the system is at a high temperature rather than at room temperature must be taken into account. The number of moles of hydrogen, n, above the sample is calculated from the ideal gas law expression

$$n = \frac{P}{R}\left[\frac{V_h}{T_h} + \frac{V_c}{T_c}\right] ,$$

where P is the pressure of hydrogen above the sample, V_h is the volume of gas at the temperature of the furnace (hot volume), T_h, and V_c is the volume at room temperature (cold volume), T_c. This, of course, assumes that the hydrogen gas is either at a temperature T_h or T_c but not at any intermediate temperature. Empirical values of V_h can be determined by introducing hydrogen gas into the apparatus (with no Zr sample present) at a temperature T_o and pressure P_o, and measuring the increased pressure, P_h, when the sample tube is heated to T_h. The hot volume can then be calculated from the relation

$$V_h = \frac{T_h}{T_h - T_c} \left[V_T - \frac{P_o V_o T_c}{P_h T_o} \right] ,$$

where V_T is the total volume occupied by the hydrogen gas at T_h, and V_o is the total volume at T_o. These are different because of the change in height of the mercury column in the manometer. The hot volume was determined as a function of T_h. It was found to remain reasonably constant with pressure at any given value of T_h.

Isotherms were obtained at 550, 600, 700, 800, and 850°C. Two hydriding runs were also made (at 600 and 800°C) by completely removing the hydrogen from the sample and then adding measured amounts from the calibrated bulbs.

D. DISCUSSION OF ERRORS

In calculating the overall hydrogen content of the sample, the maximum error was the uncertainty in room temperature, which can vary up to one degree over the "cold volume" portion of the apparatus. However, hydriding four different samples a total of ten times gave a maximum variation of only ±.003 in the H/Zr ratio. During any one run, though, the relative error between experimental points is usually less than 0.001 H/Zr.

Although the pressures on the manometer were read to ±0.1 mm and are probably accurate to within ±0.5 mm, the slight variation in the temperature of the sample leads to lower precision in the equilibrium pressure measurements. A temperature change of 0.5°C (which is within the limit of the temperature controller) can cause a pressure change of 5 mm in the steeply sloped portion of the isotherms. Actually, the variation in equilibrium pressure was usually less than 2 mm.

III. RESULTS

It was found that the maximum hydrogen-to-metal ratio which could be obtained by completely hydriding the zirconium was 1.986 ± .003. The reason for the deviation from ZrH_2 has not been established. However, deviations from stoichiometry are characteristic of transition metal hydrides. The isotherms obtained in this study are shown in Figure 3; the open circles represent dehydriding runs, and the black circles hydriding. These results are also tabulated in Tables I through V.

TABLE I

PRESSURE-COMPOSITION DATA FOR THE 850°C ISOTHERM

Pressure (mm)	H/Zr	Pressure (mm)	H/Zr	Pressure (mm)	H/Zr
731.7	1.530	716.2	1.539	422.2	1.469
577.8	1.501	579.4	1.514	398.2	1.450
479.5	1.477	487.1	1.493	386.6	1.430
409.4	1.455	437.9	1.472	400.0	1.410
397.8	1.431	765.6	1.542	390.1	1.391
402.3	1.407	614.1	1.516	389.3	1.289
406.4	1.326	511.4	1.493	553.1	1.498

TABLE II

PRESSURE-COMPOSITION DATA FOR THE 800°C ISOTHERM

Pressure (mm)	H/Zr	Pressure (mm)	H/Zr	Pressure (mm)	H/Zr
582.8	1.601	562.0	1.592	526.2	1.590
454.3	1.579	331.1	1.546	322.1	1.541
282.6	1.530	243.6	1.512	211.8	1.494
198.1	1.485	175.1	1.469	137.9	1.430
161.8	1.458	162.1	1.460	135.9	1.278
138.6	1.427	154.0	1.452	137.8	1.130
137.8	1.392	146.6	1.444	378.0	1.556
136.9	1.243	139.0	1.436	771.6	1.621
725.6	1.620	692.7	1.615	461.3	1.588

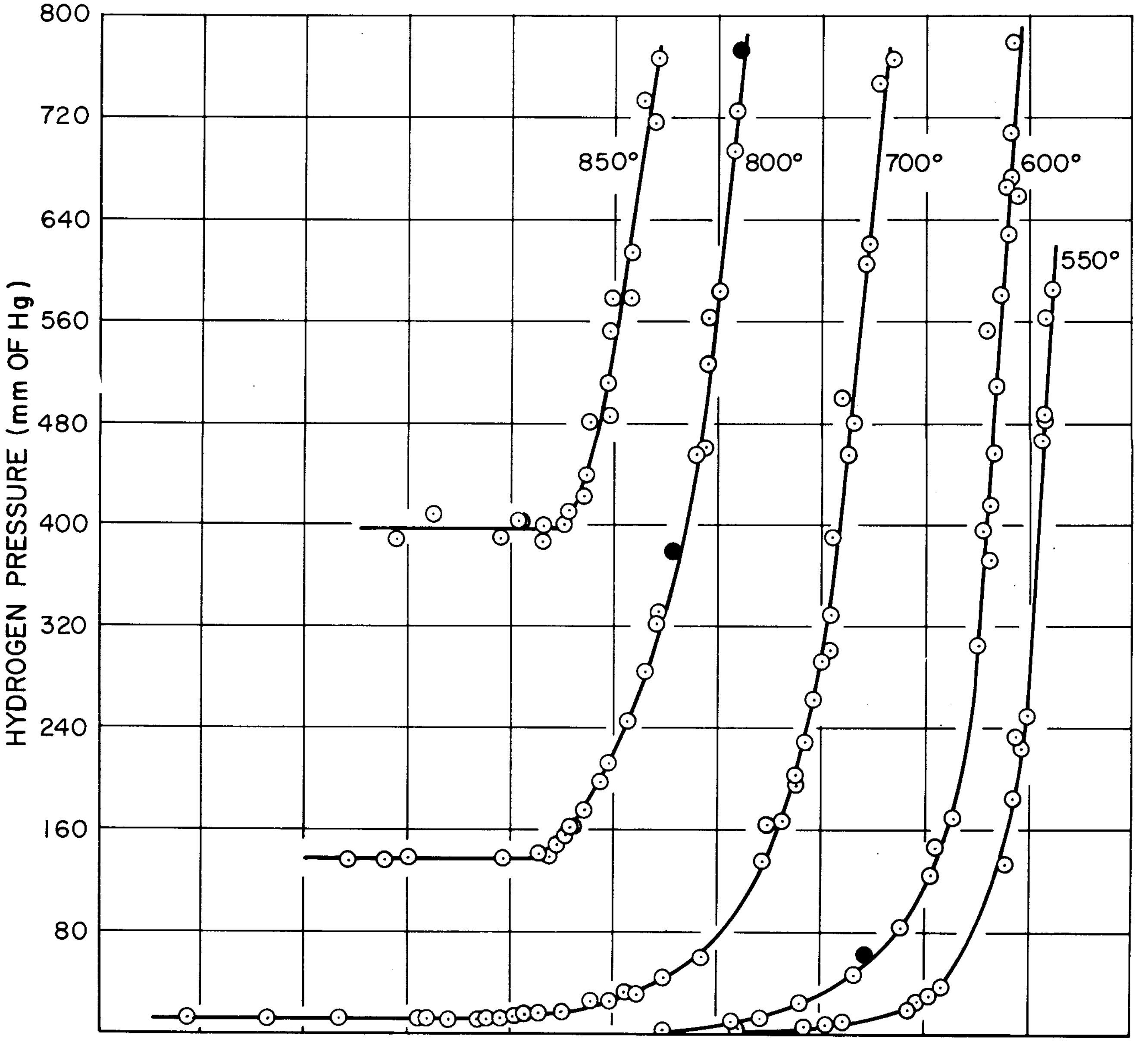

Figure 3. Pressure-Composition Isotherms of the Zr-H System

TABLE III
PRESSURE-COMPOSITION DATA FOR THE 700°C ISOTHERM

Pressure (mm)	H/Zr	Pressure (mm)	H/Zr	Pressure (mm)	H/Zr
745.8	1.757	13.0	1.376	12.8	1.389
605.3	1.743	12.0	1.232	12.0	1.368
302.1	1.707	13.0	1.085	11.6	1.339
194.4	1.675	619.1	1.745	11.7	1.310
60.2	1.583	453.8	1.725	499.1	1.719
26.1	1.497	135.2	1.643	765.1	1.768
13.6	1.402	44.6	1.547	328.4	1.708
12.0	1.318	32.9	1.511	292.3	1.700
12.3	1.163	25.4	1.479	261.6	1.692
479.1	1.730	18.3	1.450	227.9	1.683
389.6	1.711	15.7	1.426	202.3	1.674
162.5	1.648	14.7	1.412	167.2	1.661
32.8	1.521				

TABLE IV
PRESSURE-COMPOSITION DATA FOR THE 600°C ISOTHERM

Pressure (mm)	H/Zr	Pressure (mm)	H/Zr	Pressure (mm)	H/Zr
672.9	1.882	0.784	1.395	0.72	1.373
455.3	1.866	0.595	1.289	0.67	1.356
664.1	1.879	0.569	1.185	0.62	1.097
578.8	1.872	0.599	1.072	61.5	1.744
395.0	1.857	777.8	1.885	555.2	1.858
627.1	1.879	509.1	1.867	658.1	1.889
415.1	1.863	146.8	1.812	371.1	1.860
304.2	1.850	22.58	1.680	707.5	1.883
170.3	1.826	13.01	1.643	29.7	1.709
124.2	1.805	3.57	1.546	23.2	1.694
85.2	1.777	1.92	1.499	19.8	1.684
46.7	1.732	1.24	1.448	17.1	1.674
7.8	1.616	1.06	1.428	14.9	1.666
0.871	1.412	0.80	1.392	12.6	1.656

TABLE V

PRESSURE-COMPOSITION DATA FOR THE 550°C ISOTHERM

Pressure (mm)	H/Zr	Pressure (mm)	H/Zr
849.5	1.929	0.67	1.548
486.6	1.915	0.415	1.518
225.3	1.892	0.286	1.470
134.2	1.876	561.7	1.916
19.85	1.784	185.1	1.884
4.84	1.684	25.2	1.792
1.12	1.587	465.5	1.912
0.229	1.462	232.5	1.886
0.114	1.363	30.2	1.805
0.096	1.307	7.6	1.707
0.124	1.218	1.40	1.606
0.091	1.137	0.61	1.539
0.090	0.957	0.288	1.483
586.0	1.922	0.181	1.429
247.0	1.898	0.156	1.376
35.6	1.815	0.099	1.282
9.0	1.719	483.1	1.915
1.61	1.618	3.01	1.657
1.10	1.582	3.54	1.667

IV. DISCUSSION

A. $(\beta + \delta)/\delta$ PHASE BOUNDARY

As hydrogen is withdrawn from fully hydrided zirconium hydride, the equilibrium pressure decreases sharply in the single-phase δ-hydride region. When the composition at which the β-phase is formed is reached, the pressure becomes constant, giving rise to a plateau indicative of a two-phase $(\beta + \delta)$ region. The point of intersection of the plateau with the steeply sloping portion of an isotherm defines the composition at which the $(\beta + \delta)/\delta$ boundary occurs at the particular temperature of that isotherm. This point can be easily discerned for the 850 and 800°C isotherms in Figure 3. In order to do so for the 700, 600, and 550°C isotherms, the relevant portions have been replotted on expanded scales as seen in Figures 4 through 6. The position of the $(\beta + \delta)/\delta$ boundary as a function of temperature is shown in Table VI and Figure 7.

TABLE VI

POSITION OF $(\beta + \delta)/\delta$ BOUNDARY

Temperature (°C)	Boundary (H/Zr)
550	1.33
600	1.33
700	1.36
800	1.43
850	1.45

The boundary obtained in the present study does not agree with any of the previous three[1,3,5] investigations shown in Figure 1. It falls between the boundary of Vaughan and Bridge, and that of Edwards et al. The boundary given by Vaughan and Bridge was deduced from an X-ray study and depends on estimating its position between two regions containing points representing the phases present rather than determining actual points on the boundary. In addition, a phase present in low concentration cannot be detected by X-ray diffraction analysis, thereby shifting the boundary toward the hydrogen-poor side of the phase diagram.

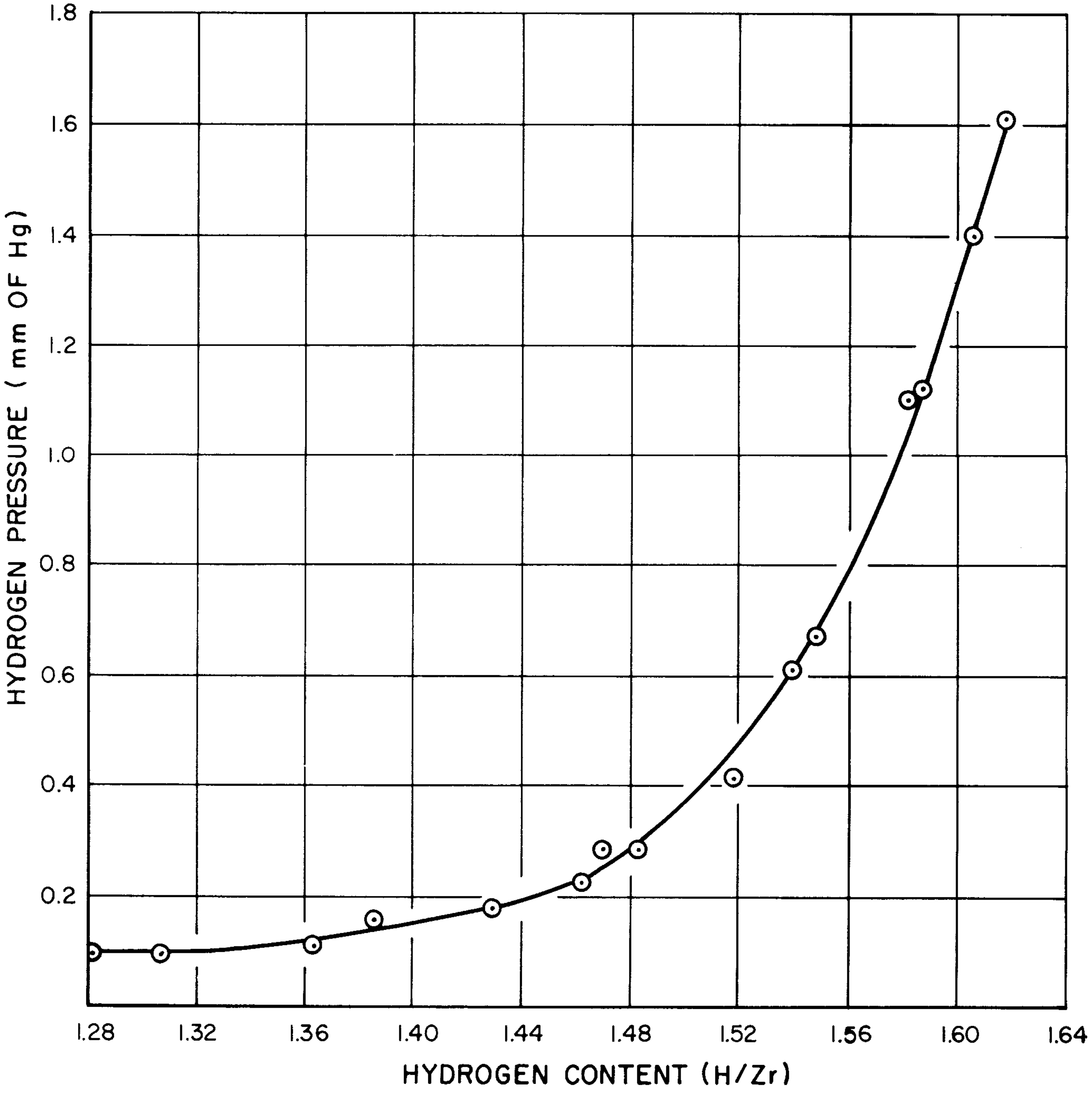

Figure 4. 550°C Isotherm

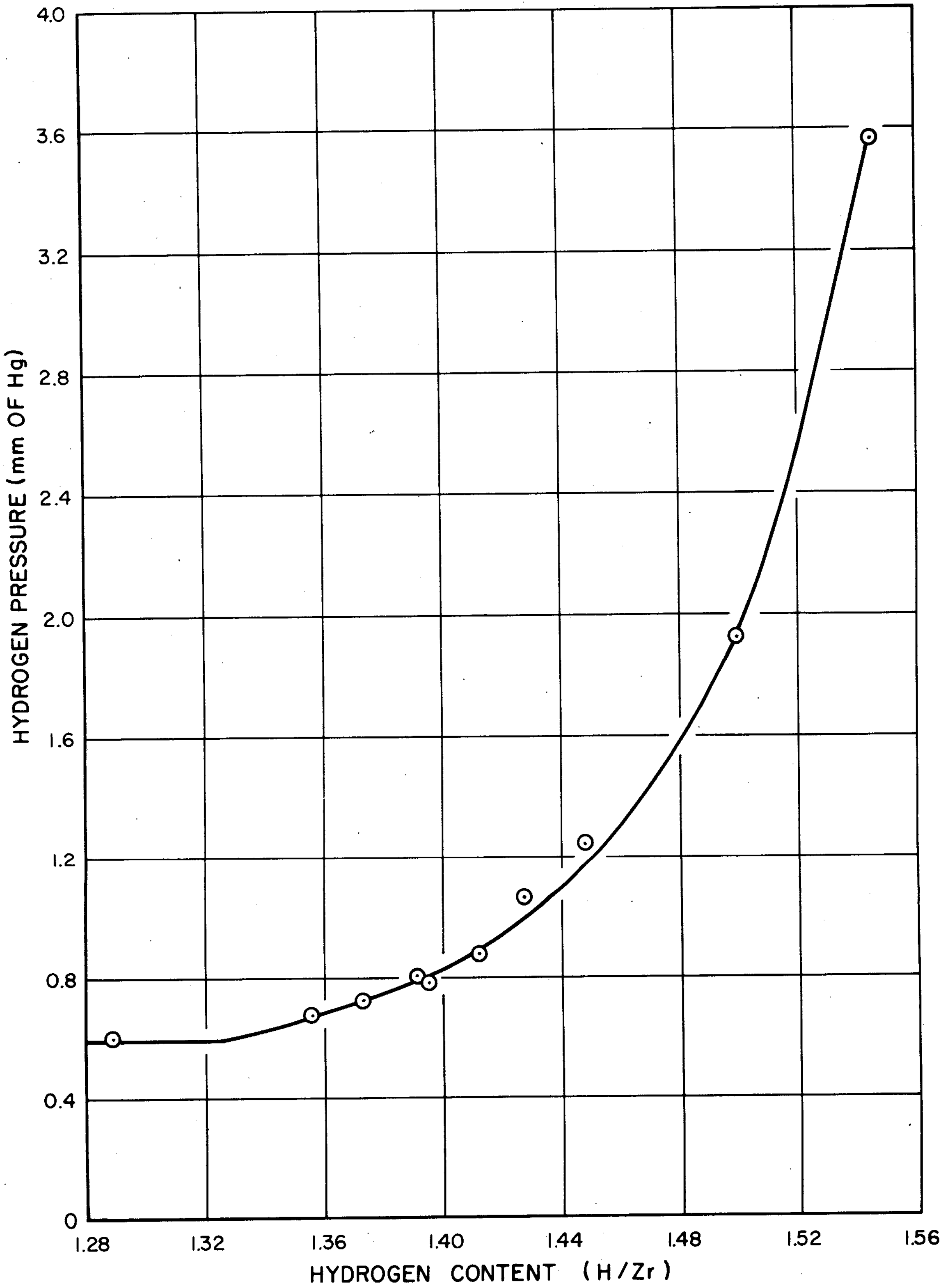

Figure 5. 600°C Isotherm

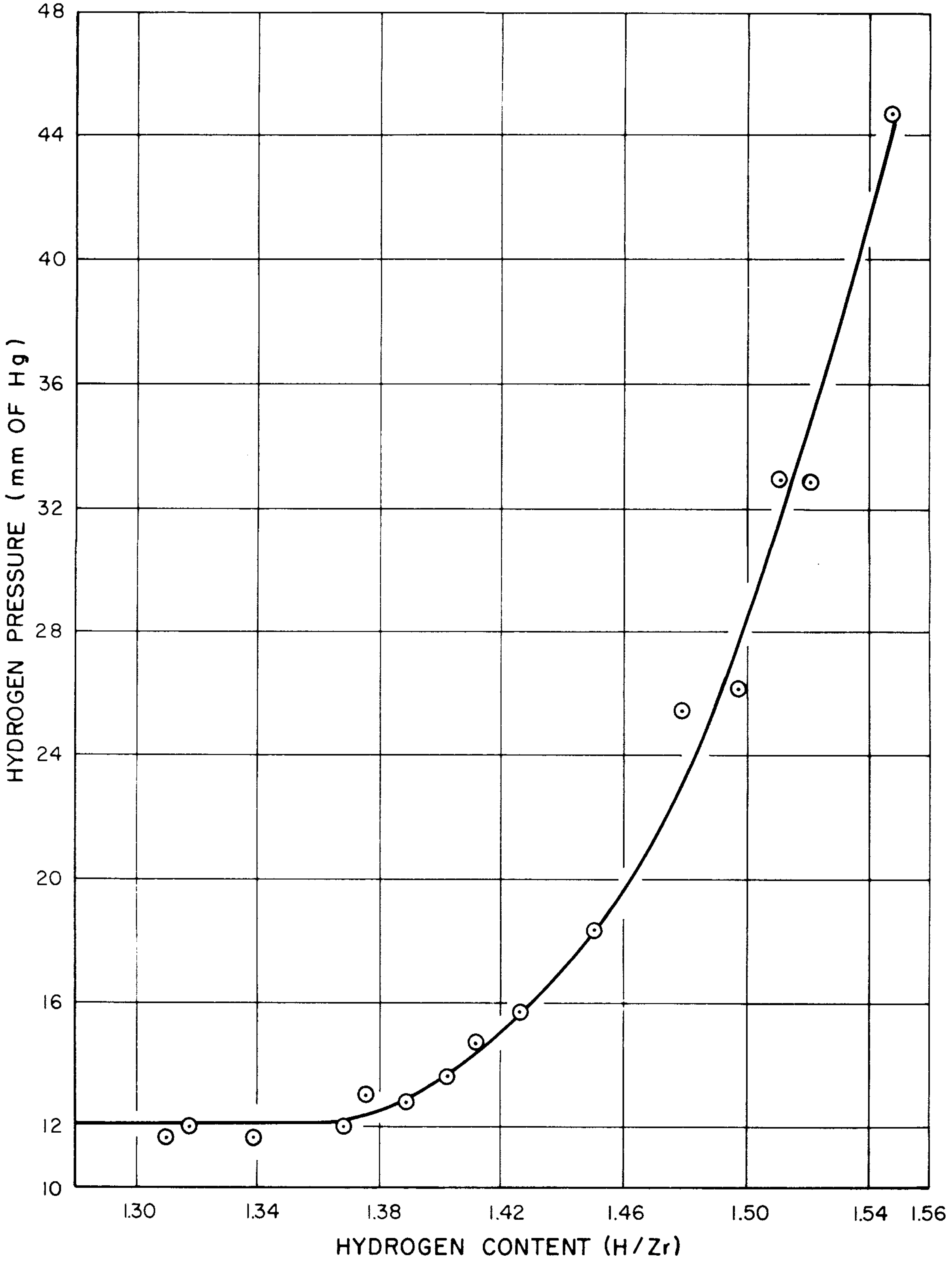

Figure 6. 700°C Isotherm

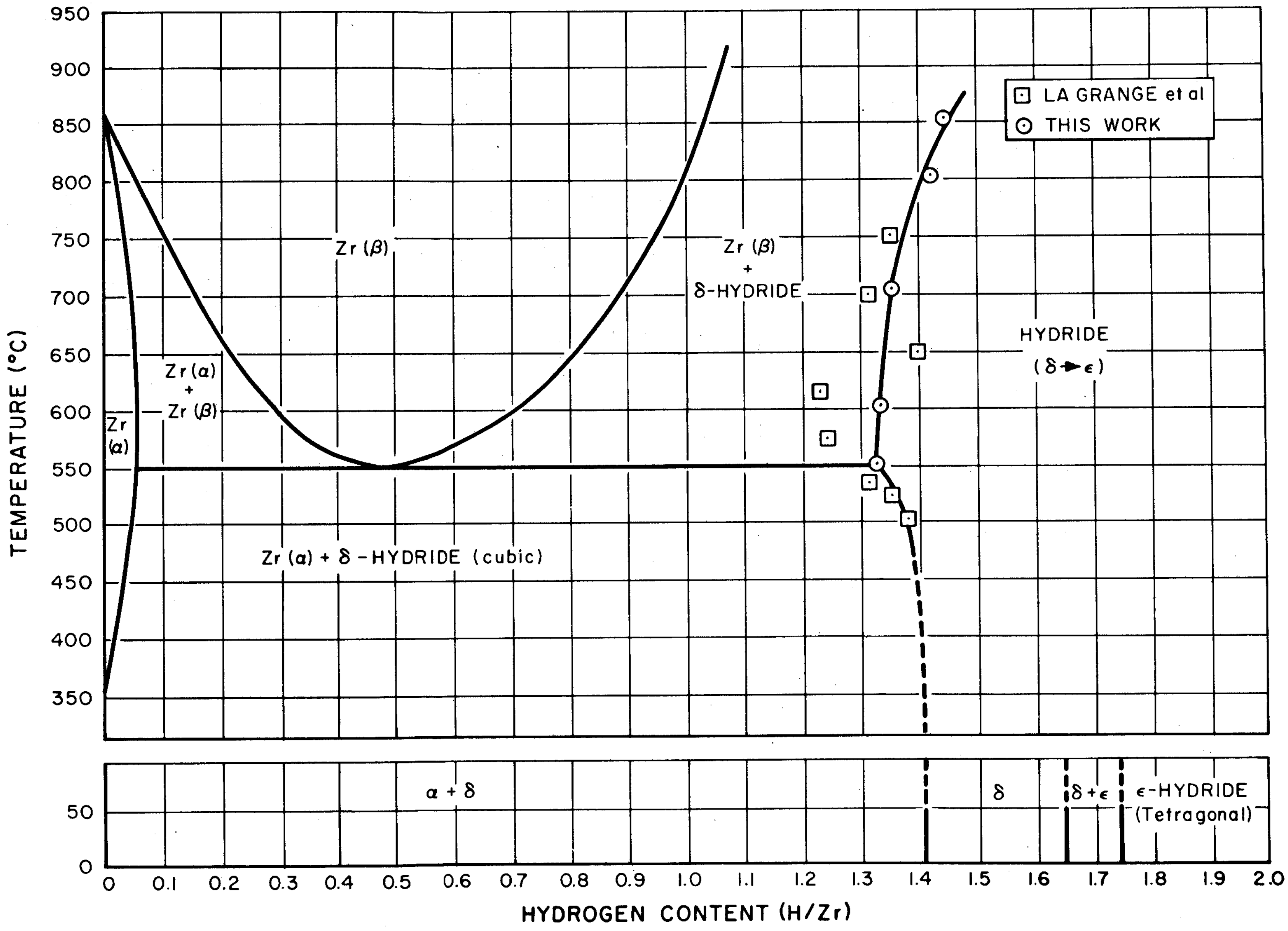

Figure 7. Modified Zirconium-Hydrogen Phase Diagram

The zirconium sample used by Hall, Martin, and Rees contained a large concentration of oxygen impurity (0.4 wt %), which should have a considerable effect on the uptake hydrogen. The negative slope of this boundary is opposite to what would be expected in such a phase diagram. The reason for the difference between the present investigation and that of Edwards et al is not clear, although the zirconium sample used in the present work was hafnium-free and purer in oxygen than Edwards' sample by a factor of ten. The single-phase region of these isotherms has much steeper slopes than those of Edwards. A recent study of this system by La Grange et al[11], published shortly before the completion of this work, gives fair agreement with the boundary established in this investigation. Their data ranges from 500 to 750°C, and, as seen in Figure 7, it is scattered about the boundary obtained in the present study. Since they did not obtain as many pressure-composition points on the isotherms, the intersection of the plateau region with the steeply sloping region could not be as precisely defined as in the present study.

B. $\delta + \epsilon$ TWO-PHASE REGION

As mentioned above, there is some question as to the existence and range of a two-phase ($\delta + \epsilon$) region. Figure 8 is a compilation of all known room temperature X-ray data plotted as c/a ratio vs hydrogen content. From the end of the two-phase ($\alpha + \delta$) region to H/Zr = 1.646, only the cubic δ-phase is observed[5,9,12,13] (c/a = 1) with a lattice parameter of a = 4.78 Å. From H/Zr = 1.66 to 1.70, two phases were observed,[9,12] the cubic δ-phase and a tetragonal phase, designated as ϵ, having a c/a ratio equal to about 0.931 ± .002.

Thus, we see from Figure 8 that there is a narrow two-phase ($\delta + \epsilon$) region extending from about H/Zr = 1.65 to 1.72 ± .02. As the hydrogen content is increased beyond this two-phase region, the c/a ratio of the ϵ phase decreases[5,9,13] from 0.931 to about 0.894 at a H/Zr ratio of 1.88. From H/Zr = 1.88 to 2, the c/a ratio remains constant[9,12,14-16] at 0.894.

In the present pressure-composition-temperature study, no evidence of a two-phase ($\delta + \epsilon$) region was observed in the 550 to 850°C temperature range. If these two phases coexisted in this temperature range, there would be an additional plateau, or a break in the continuity of the isotherms. That this is not the case can be seen from Figure 3, and Figures 9 and 10 which are expanded scale

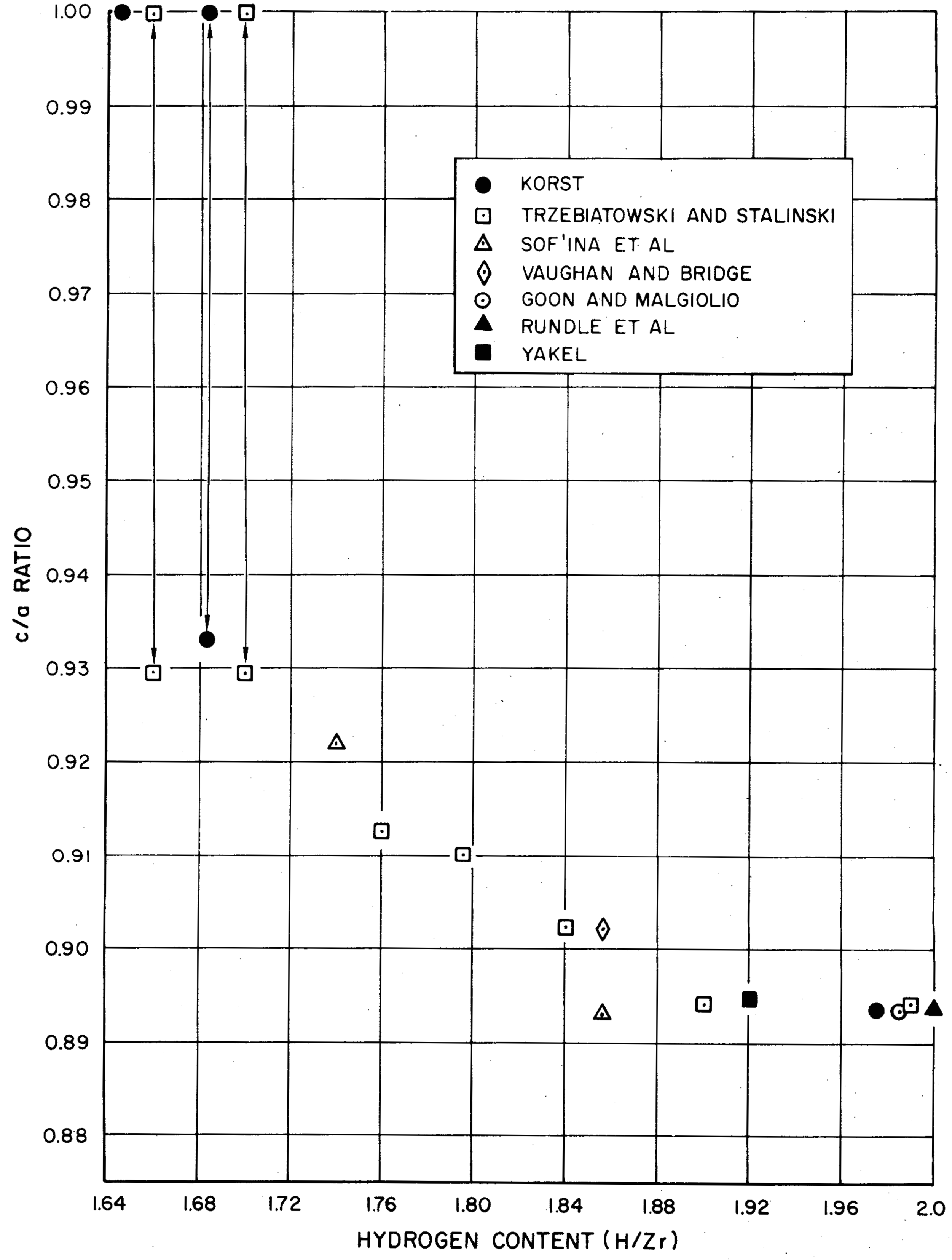

Figure 8. Variation of c/a Ratio with Hydrogen Content

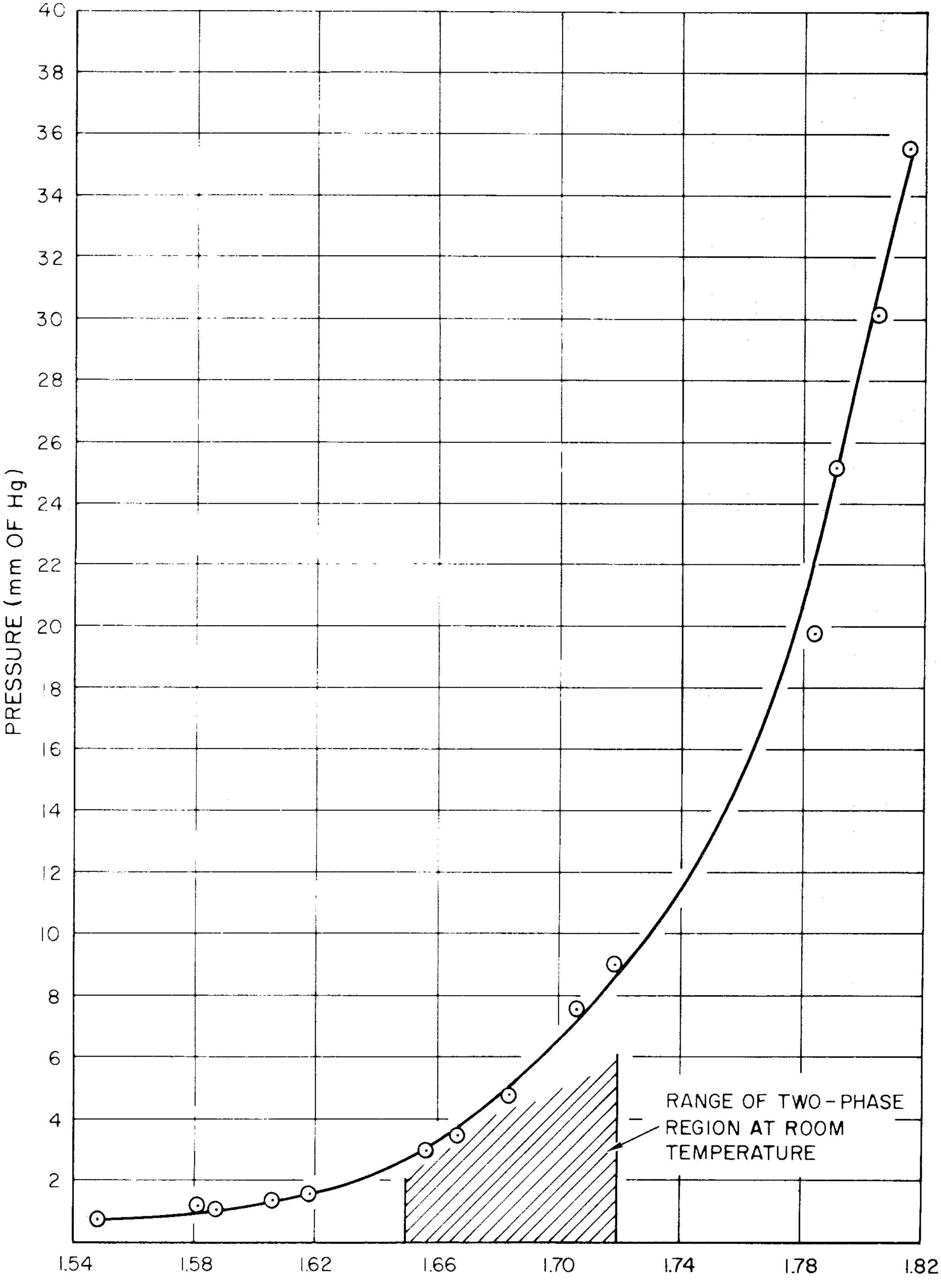

Figure 9. 550°C Isotherm

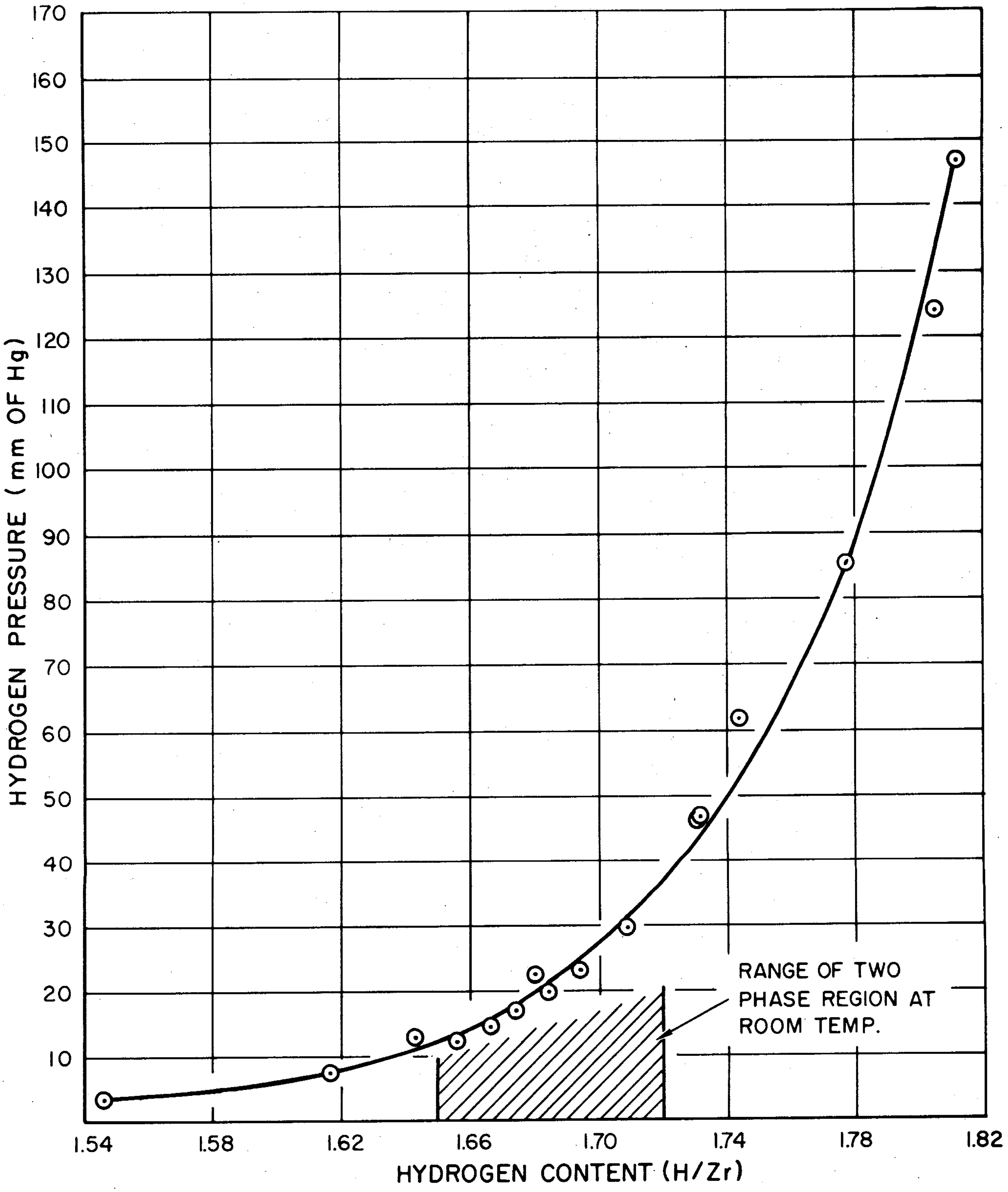

Figure 10. 600°C Isotherm

plots of the 550 and 600°C isotherms including the region where the $(\delta + \epsilon)$ phase was present at low temperatures. It appears, therefore, that the two-phase $(\delta + \epsilon)$ region must become narrower with increasing temperature, disappearing entirely somewhere between room temperature and 550°C. In Figure 7, the $(\delta + \epsilon)$ region is shown at low temperatures, while at elevated temperatures there is probably a continuous second order transition from the δ-cubic phase to the tetragonal ϵ-phase.

REFERENCES

1. M. N. A. Hall, S. L. H. Martin, and A. L. G. Rees, Trans. Faraday Soc. 41 (1944) p 306
2. E. A. Gulbransen and K. F. Andrew, J. Metals 7 (1955) p 136
3. R. K. Edwards, P. Levesque, and D. Cubicciotti, J. Am. Chem. Soc. 77 (1955) p 1307
4. C. E. Ells and A. D. McQuillan, J. Inst. Metals 85 (1956) p 89
5. D. A. Vaughan and J. R. Bridge, J. Metals 8 (1956) p 528
6. M. W. Mallett and W. M. Albrecht, J. Electrochem. Soc. 104 (1957) p 142
7. T. B. Douglas, J. Am. Chem. Soc. 80 (1958) p 5040
8. E. A. Gulbransen and K. F. Andrew, J. Electrochem. Soc. 101 (1954) p 474
9. W. Trzebiatowski and B. Stalinski, Rocznicki Chem. 30 (1956) p 691
10. D. Whitwham, M. A. Huber, J. Herenguel, Acta Met. 7 (1959) p 65
11. L. D. La Grange, L. J. Dykstra, J. M. Dixon, and U. Merton, J. Phys. Chem. 63 (1959) p 2035
12. W. L. Korst (to be published)
13. Sof'ina, Z. M. Azarkh, and N. N. Orlova, Kristallografiya 3 (1958) p 539
14. E. J. Goon and J. Malgiolio, AEC Report NYO-7547 (April 1958)
15. R. E. Rundle, C. G. Shull, and E. O. Wollan, Acta Cryst. 5 (1952) p 22
16. H. L. Yakel, Jr., Acta Cryst. 11 (1958) p 46