EQUILIBRIUM DISSOCIATION PRESSURES
OF THE
DELTA AND EPSILON PHASES
IN THE
ZIRCONIUM-HYDROGEN SYSTEM

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ABSTRACT

Pressure-temperature isochores were obtained for zirconium-hydrogen alloys, spanning the H/Zr^* composition range of 1.430 to 1.910. The studies were confined to the temperature limits of 300 to 900°C, and the pressure limits of 0.01 to 10.0 atm. An expression equating equilibrium dissociation pressure to temperature and composition was determined, as was the heat of solution function over the range of composition studied. Based on the results of the study, a modification to the zirconium-hydrogen binary phase diagram was proposed, involving construction of a single line, extending upward in temperature from the $ZrH_{1.59}$ composition, denoting onset of the $\delta \rightarrow \epsilon$ transformation, in place of the two-phase ($\delta + \epsilon$) region appearing on recent diagrams. It is considered that the two-phase region exists only in ternary or higher-order alloy systems, generally resulting from contamination with oxygen, carbon, or nitrogen.

* H/Zr - the atom ratio of hydrogen to zirconium

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I. INTRODUCTION

While the zirconium-hydrogen constitution diagram has, in general, been quite adequately defined in previous investigations,¹⁻¹⁵ contradictory results in the isochores presented by Gilbert⁶ and Vetrano and Atkins,¹² and in subsequent work of Atkins¹³ and the isotherm data of Libowitz,¹⁸ indicate incomplete definition of the pressure-composition-temperature (P-C-T) relationships in the δ - ϵ region of the binary. Exact knowledge of the P-C-T relationships in these regions is of great significance, as this information is directly involved in the determination of the SNAP reactor fuel parameters: hydrogen redistribution, dissociation pressure-cladding strength relationships, etc. The investigation was undertaken in an attempt to establish more definitely the P-C-T relationships for the δ - ϵ phases.

Quantitative representation of the dissociation pressure can best be accomplished by means of an equation of the general form

$$\log P = K_1 + K_2/T, \quad \dots(1)$$

T being the absolute temperature, K_1 , a factor expressing the pressure dependence of the solubility of the gas in the solid phase, and K_2 , a coefficient relating to the heat of solution of the gas in the solid phase.

From a plot of log pressure vs reciprocal temperature, the functional relationship between Equation 1 and the composition parameter (X) may be determined (X representing, in this system, the hydrogen-to-zirconium atom ratio). The general equation for the family of curves (isochores) expressing this relationship is given by

$$\log P = A + B X - \frac{C}{T}, \quad \dots(2)$$

where A, B, and C are constants, the other parameters retaining their previous identities.

Regarding the isochore plot, C, the heat of solution coefficient, may be determined from the slope of the isochores; a necessary requisite for a constant heat of solution being an invariant isochore slope, for the concentrations considered. Conversely, a variation in slope necessarily implies a concentration

dependence of the heat of solution. The solute concentration or solubility dependence on pressure (i.e., coefficient B in Equation 2) is evidenced in the spacing of the isochores, pressure-dependent solubility giving rise to nonuniform spacing of isochores of equal increments of composition.

Considering once again Equation 2, if X is plotted vs log P, at constant temperature, the slope of the resulting curve or isotherm defines the coefficient B.* The slope of the isotherms so plotted relates to the physical mechanism of solution of the gas in the solid phase. In dilute solution (i.e., $X \cong 0$), the slope is 2, indicating that dissolution of hydrogen in zirconium is atomic, rather than molecular, in nature. This is as would be predicted from Sievert's law for a bimolecular gas. The implication is that, at constant temperature, the concentration of hydrogen in the solid phase will be proportional to the square root of the ambient hydrogen pressure. To the extent that concentration dependence on pressure obeys this relationship, the activity coefficient of hydrogen dissolved in the solid phase will be constant at unity. However, departure from ideality (i.e., the isotherm slope $\neq 2$) will result when, due to increasing solute concentration, the activity coefficient departs from unity. A change in slope or deviation from linearity of the isotherms, or a change of spacing of the isochores, may then be interpreted as a concentration dependence of the activity of hydrogen in solid solution.

The major area of disagreement in the works of Gilbert,⁶ Vetrano and Atkins,¹² and the subsequent work of Atkins¹³ lay in the spacing of the isochores of the δ - ϵ region, relative to the two-phase β - δ equilibrium line. Specifically, the isochores of Vetrano and Atkins, and Gilbert (see Figure 1), exhibited a progressively increasing change in spacing with increasing hydrogen concentration (i.e., B continuously increasing with hydrogen concentration, in Equation 2). However, Atkins, in his subsequent work, reported an isochore map that would require anomalous behavior of the activities in this region (i.e., the condensing of the isochores at compositions between $ZrH_{1.6}$ and $ZrH_{1.75}$) (see Figure 2).

While such behavior would be inconsistent in a true binary one-phase region, it must be considered that two distinct phases, (fcc) δ and (fct) ϵ , coexist^{9-11,14-16} over the composition range of approximately 1.65 to 1.75 H/Zr (see Figure 3).

*The heat of solution must be independent of concentration, for this to be strictly true.

Figure 2. Isochore Diagram (Atkins¹³)

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Figure 3. Zirconium-Hydrogen Phase Diagram
(Libowitz¹⁴)

Although available evidence indicates that the two-phase $\delta + \epsilon$ equilibrium does not exist much above room temperature, one may postulate that a "memory-effect" of the $\delta + \epsilon$ low-temperature equilibrium resulted in the apparently anomalous behavior of the activity coefficient (isochore spacing) reported by Atkins.¹³ This analysis becomes especially significant, in light of the fact that Edwards and Levesque,¹⁶ in their studies on the ternary system, zirconium-oxygen-hydrogen, report that the extent of the δ - ϵ two-phase region is relative to the oxygen concentration. Atkins reported the average oxygen content of his hydrided samples to be considerably higher than that of the starting materials, which was given as 0.10 wt %. The zirconium samples used by Gilbert contained 0.005 wt % O.

TABLE 1
CHEMICAL COMPOSITION OF MELT STOCK

Element	ppm	Element	ppm	Element	ppm
Al	40	Cu	<20	Ni	<10
B	<0.5	Fe	370	P	70
C	<10	H	54	Pb	8
Ca	<20	Li	<3	Si	35
Cd	<0.3	Mg	<100	Sn	<50
Cl	97	Mn	20	Ti	<20
Co	<5	Mo	<10	V	<10
Cr	34	Na	<15	W	<40
				Zn	<25

TABLE 2
COMPOSITION OF HYDRIDED SPECIMENS

Specimen Number	Hydrogen (H/Zr)*		Oxygen (ppm)	Carbon (ppm)	Nitrogen (ppm)
	By Weight Gain	By Vacuum Fusion			
J-14	1 431	1 47-1 57	300-800 400-1400	200-800 200-800	30-50 30-300
J-59	1 460				
J-64	1 477				
J-16	1 482	1 56-1 57			
J-30	1 527				
J-42	1 541				
J-24	1 542	1 57-1 60			
J-60	1 556				
J-34	1 577				
J-48	1 609	1 62-1 63			
J-18	1 641				
J-46	1 661				
J-49	1 678	1 68-1 75			
J-35	1 703				
J-3	1 710				
J-52	1 724	1 70-1 74			
J-19	1 734				
J-33	1 751				
J-43	1 781	1 67-1 87			
J-32	1 804				
J-4	1 810				
J-37	1 845	1 69-1 89			
J-2	1 860				
J-38	1 868				
J-5	1 890	1 85-1 89			
J-57	1 903				
J-61	1 908				
J-39	1 915	1 77-1 89			
Typical before hydriding					
Typical after hydriding					

*H/Zr is the atom ratio of hydrogen to zirconium.

II. EXPERIMENTAL

A. MATERIALS AND PREPARATION

All specimens used in this investigation were prepared by double consumable-electrode arc-melting of compacted reactor grade zirconium sponge. Chemical analyses of the melt stock and hydrided specimens are given in Tables 1 and 2. Subsequent to extrusion and swaging to 1/2 in. in diameter, the rod was machined to 3/8 in. in diameter, to minimize surface contamination, and then cut into 1-in. cylinders. These were chemically polished* and vacuum annealed at 950°C and 10^{-5} torr for 24 hr, to eliminate possible error due to the presence of volatile constituents. The samples were then repolished, weighed, and identified. Hydriding was accomplished by adding calibrated amounts of pre-purified hydrogen† to the specimen contained in an evacuated retort at 900°C. This was followed by furnace cooling to room temperature. After hydriding, the samples were reweighed, compositions calculated, and all data recorded.

B. PROCEDURE

The dissociation pressure data were obtained with the isochore apparatus, shown in Figure 4. The hydrided samples, approximately 3/8 in. in diameter by 1 in. long, were placed in the mullite sample chamber. Solid mullite rod was then inserted above the specimen in the chamber to minimize void volume, and the retort was evacuated to $< 1\mu$. Subsequent to evacuation, the retort was isolated, the pressure sensing transducer system was zeroed, and the retort was inserted in a wire-wound resistance furnace and brought up to temperature. Specimen temperature was measured with a Chromel-Alumel thermocouple, located in the heat sink, outside and adjacent to the retort wall and positioned at the sample midspan. When equilibrium had been established, pressure and temperature data (in terms of output voltages of the pressure transducer and thermocouple) were recorded, and the operation repeated at other temperatures. The retort was alternated between two furnaces during a run to confirm the

*45 H₂O, 45 HNO₃, 10 HF (vol%)

† < 10 ppm total impurities

a. Photograph

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b. Schematic

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Figure 4. Isochore Apparatus

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reliability of the temperature data. Subsequent to testing, samples were submitted for the determination of hydrogen, oxygen, nitrogen, and carbon content.

C. DISCUSSION OF ERRORS

The major sources of error encountered in this investigation were:

- 1) Nonisothermal specimen environment
- 2) Accuracy of temperature measurement
- 3) Accuracy of pressure measurement
- 4) Gas permeation and leakage under pressure and vacuum
- 5) Uncertainty in hydrogen concentration of sample
- 6) Actual void volume of the "null-void" system.

Regarding the first of these, nonisothermal specimen environment, this effect was minimized through the use of a massive stainless steel heat sink (see Figure 4b). Maximum temperature variation, as measured in a mockup specimen, was determined to be $< 0.5^{\circ}\text{C}$.

The precision of temperature measurement was $\sim 1^{\circ}\text{C}$, as limited by thermocouple calibration. However, the procedure employed in each run, involving determination of data at many temperatures and in two identical isochore apparatus, served to statistically minimize temperature error.

Regarding pressure measurement, the accuracy and precision of the pressure data, as measured with strain-gage transducers and a precision potentiometer, was determined to be ± 0.1 psia. This was statistically minimized by making many determinations on each sample.

In order to determine the extent to which gas permeation and leakage, under pressure and under vacuum, would influence the data, preliminary runs were made, under vacuum and under pressure, over the temperature interval investigated. A stainless steel specimen was used, to maintain similar test conditions. The results of these determinations are shown in Figure 5. As may be seen from these curves, significant error may be introduced, should the test extend over long periods of time (1) at temperatures above 700°C when under pressure, and (2) above 600°C under conditions of

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Figure 5. Retort Permeation and Leakage Under Pressure and Under Vacuum

partial vacuum. Based on these results, each individual test was planned so as to minimize introduction of error due to these sources. Since error due to these sources must introduce nonlinearity in a plot of log pressure vs reciprocal temperature, we may conclude that it was essentially absent, since nonlinearity was not observed.*

By far the greatest single source of error was due to the uncertainty in the hydrogen concentration of the individual samples. Because of the inadequacy of hydrogen analysis, by the vacuum fusion technique, in meeting the required degree of precision (see Table 2), the weight gain of the hydrided specimens was accepted as defining hydrogen composition. While care was exercised to minimize contamination which would result in erroneous compositions, as computed from weight gain data, a slight discoloration was apparent on the surfaces of all specimens after hydriding. The film could be interpreted as

*Exclusive of deviation from linearity due to void volume considerations, as will be discussed in a subsequent paragraph.

contamination of the sample with oxygen and/or nitrogen as a surface film, and possibly as dissolved interstitial solid solutions. While the apparent degree of contamination was slight, in all instances, the relative atomic weights of oxygen and nitrogen, as compared to hydrogen, magnify the error significantly. However, the influence on dissociation pressure of the variation in interstitial impurity concentration between samples apparently lay within experimental error, since relative displacement of the isochores was not in evidence. The least-squares computer program, used for final determination of the isochore plot and the dissociation pressure equation, undoubtedly served to minimize the effect of data scatter due to nonuniform concentrations of these impurities in individual samples.

Under certain conditions, the presence of a void volume in the sample chamber could introduce considerable error. However, compensation for the error involved can be made, if the void volume of the retort is known accurately at some temperature, and an expression relating the change in this volume to temperature has been determined. The void volume of both retorts used in this experiment was 15.6 cc at 22°C. The temperature-volume relationship was determined by: (1) loading a stainless steel sample in the retorts under identical test conditions, (2) adding a known pressure of hydrogen at the reference temperature (22°C), (3) heating the isolated retort, and (4) recording retort pressure as a function of temperature. Since initial pressure, temperature, and volume are known, the molar hydrogen content of the retort may be calculated from the gas law:

$$P_0 V_0 = n_0 R T_0 \quad \dots (3)$$

$$n_0 = \frac{P_0 V_0}{R T_0} \quad \dots (4)$$

It then follows that, since the retort was isolated before heating (i.e., $n_0 = \text{constant} = P_0 V_0 / R T_0$), the volume may be determined from the relation between specimen temperature and retort pressure, at temperature t , as follows:

$$P_t V_t = n_t R T_t \quad \dots (5)$$

Since

$$n_t = n_0 = \frac{P_0 V_0}{RT_0} = \text{constant} \quad , \quad \dots (6)$$

$$P_t V_t = CT_t \quad , \quad \dots (7)$$

or

$$V_t = C \frac{T_t}{P_t} \quad . \quad \dots (8)$$

It should be noted that V_t is not the true expression for volume, but rather that fiducial volume that would be applicable in the ideal gas law, were the entire retort volume at specimen temperature, rather than under a gradient ranging from specimen temperature to room temperature. We shall term this fiducial volume the "equivalent volume" (V'). The change in equivalent volume as a function of temperature, for the systems used in this experiment, was found to obey the equation

$$V' = (2.97 + 0.042 T) \times 10^{-3} \quad , \quad \dots (9)$$

where (T) is the specimen temperature, expressed in degrees Kelvin.

Correction for dissociation of hydrogen to the void can then be accomplished by applying the relation given in Equation 9 to the following expression:

$$(H/Zr)_T = (H/Zr)_0 - \frac{2 PV'_T}{RTN_{Zr}} \quad , \quad \dots (10)$$

where:

$(H/Zr)_T$ = the atom ratio of hydrogen to zirconium in the sample after dissociation of hydrogen to the void at temperature T

$(H/Zr)_0$ = the hydrogen-to-zirconium atom ratio of the sample at the temperature T = 273°K (i.e., the "as-hydrided" atom ratio of the sample)

P = the retort pressure (atm)

T = the specimen temperature($^{\circ}\text{K}$)

N_{Zr} = the number of gram atoms of zirconium in the sample

R = the gas constant $\left(0.08205 \frac{\text{l-atm}}{\text{deg-mole}}\right)$

V'_T = the apparent volume at temperature T (l)

Analyzing this equation, the last term is a direct measure of the extent to which hydrogen has dissociated to the void. This term, when compared to the magnitude of the atom ratios, permits evaluation of the relative error introduced through a zero void volume assumption. Since the overall accuracy of the experiment might reasonably be approximated by an uncertainty of ± 0.0025 in the atom ratio, the assumption of a zero void volume would introduce significant error when the term representing dissociation to the void exceeds 0.005, or when

$$\frac{2PV'_T}{RTN_{\text{Zr}}} > 0.005 \quad \dots(11)$$

Since R and N_{Zr}^* are constants and V'_T is a function of T (from Equation 9), this expression may be rewritten in the form

$$P\left(\frac{288}{T} + 0.042\right) > 0.0225 \quad \dots(12)$$

Solution of this expression for the temperature limits of the experiment from 500 to 900°C shows that, for pressures in excess of ~ 0.5 atm, significant error may be introduced through assumption of a zero void volume.

This uncertainty above ~ 0.5 atm was taken into consideration when assigning significance to the data.

*Since sample size was very nearly constant at 10 g, $N_{\text{Zr}} = \frac{10}{91.22} \cong 0.11$.

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Figure 6. Pressure-Temperature-Composition Data for Zirconium Hydride

III. RESULTS

The isochores determined in this study, relating dissociation pressure, temperature, and composition of the δ and ϵ phases in the zirconium-hydrogen binary, are shown in Figure 6. These data are also tabulated in Table 3. An isochore map, constructed from results obtained from a least-squares fit of the data, is presented in Figure 7.

TABLE 3

PRESSURE-TEMPERATURE-COMPOSITION DATA FOR DELTA-EPSILON ZIRCONIUM HYDRIDE

Sample	H/Zr	Temperature (°C)	Pressure (atm)	Temperature (°C)	Pressure (atm)	Sample	H/Zr	Temperature (°C)	Pressure (atm)	Temperature (°C)	Pressure (atm)		
J-14	1.431	738	0.045	856	0.600	J-3	1.710	608	0.0604	654	0.182		
		767	0.087	864	0.711			617	0.0737	677	0.301		
		777	0.113	883	1.054			630	0.104	687	0.374		
		796	0.170	893	1.260			653	0.176	699	0.468		
		806	0.207	941	3.030	J-19	1.734	586	0.050	643	0.226		
		826	0.325	952	3.780			616	0.112				
		834	0.381										
J-59	1.460	754	0.0800	780	0.1392	J-33	1.751	615	0.124	671	0.450		
		766	0.1046					646	0.257				
J-64	1.477	726	0.0576	749	0.0902	J-43	1.781	607	0.137	653	0.434		
J-16	1.482	680	0.0210	766	0.146	J-32	1.804	616	0.170	644	0.567		
		709	0.0425	882	1.060			595	0.171			674	1.065
		740	0.0820	904	1.590			616	0.289			676	1.115
				643	0.547								
J-30	1.527	703	0.0477	713	0.0608	J-4	1.810	523	0.0249	596	0.219		
J-42	1.541	686	0.0373	698	0.0496			550	0.0589	603	0.252		
								575	0.121	614	0.351		
								577	0.127	640	0.636		
J-24	1.542	685	0.043	827	0.689	J-37	1.845	589	0.169	641	0.651		
		712	0.077	850	1.019			550	0.0945	647	1.081		
		736	0.126	882	1.68			611	0.498				
		765	0.224	912	2.58								
		794	0.392	940	3.69								
J-60	1.556	698	0.0634	725	0.1111	J-2	1.860	540	0.0778	588	0.311		
		723	0.1017	755	0.2055			545	0.0922	601	0.449		
J-34	1.577	671	0.0354	727	0.1218			570	0.186	613	0.608		
		699	0.0660					584	0.283	613	0.602		
J-48	1.609	695	0.0830	725	0.1628	J-38	1.868	557	0.185	598	0.555		
J-18	1.641	607	0.020	720	0.260	J-5	1.890	569	0.384	595	0.718		
		656	0.065	746	0.439			581	0.515				
		689	0.141	778	0.730	J-57	1.903	511	0.114	550	0.328		
J-49	1.678	674	0.138	728	0.296	J-61	1.908	534	0.206	568	0.526		
		701	0.232					491	0.0705	556	0.490		
J-46	1.661	617	0.0400	645	0.0815	J-39	1.915	553	0.436	508	0.190		
J-35	1.703	646	0.115	671	0.201			479	0.0731				
J-52	1.724	643	0.133	670	0.241			492	0.117	534	0.396

7635-4708
 Figure 7. Dissociation Pressure
 Isochores of Zirconium Hydride
 (Expressed as H/Zr
 atom ratios)

1

2

3

4

5

IV. DISCUSSION

The dissociation pressure equilibria of the zirconium-hydrogen binary in the δ and ϵ regions, represented by the isochores of Figure 7, may be expressed in terms of temperature and composition by the relation

$$\log P = K_1 + \frac{K_2 \times 10^3}{T} \quad \dots (13)$$

where:

$$K_1 = -3.8415 + 38.6433 X - 34.2639 X^2 + 9.2821 X^3$$

$$K_2 = -31.2982 + 23.5741 X - 6.0280 X^2$$

P = pressure (atm)

T = temperature ($^{\circ}$ K)

X = hydrogen-to-zirconium atom ratio

This equation form was given preference to that involving separation of K_1 in terms of $A + BX$, as expressed in Equation 2, since the heat of solution coefficient (K_2) was determined to be concentration dependent. That is, since $K_2 = f(X)$, B would not define the slope of the isotherm, as discussed previously (see page 9), and therefore apparently would not contribute physical significance to the dissociation pressure equation.

Considering first the coefficient K_2 of Equation 13, we may conclude that the partial molal heat of solution is not constant within the δ and ϵ regions of the binary, but rather decreases continuously with increasing hydrogen concentration, across both the δ and ϵ regions. A plot of the heat of solution coefficient as a function of hydrogen concentration, as derived from the isochore plot (Figure 7), is presented as Figure 8. From this plot, it may be seen that the heat of solution of hydrogen in the hydrided phase decreases, with increasing solute concentration, but at a decreasing rate, attaining a limiting value of ~ 8.26 for a saturated solution of limiting composition $H/Zr = 2$.

In terms of actual molal quantities, obtained by multiplying K_2 by the natural log conversion and the gas constant, the partial molal heat of

7635-4709

Figure 8. Heat of Solution Coefficient (K_2) of Zirconium Hydride as a Function of Hydrogen-to-Zirconium Atom Ratio (X)

7635-4710

Figure 9. Solubility Coefficient (K_1) of Zirconium Hydride as a Function of Hydrogen-to-Zirconium Atom Ratio (X)

solution of hydrogen in the hydride decreases from -46.3 kcal/mole, in δ of composition $\text{ZrH}_{1.4}$, to -37.7 kcal/mole, in ϵ of composition $\text{ZrH}_{1.9}$. Of significance is the fact that no discontinuity in the function is in evidence throughout the entire δ and ϵ composition range. This is not as would be expected if the $\delta \rightarrow \epsilon$ transformation were of first order, but is entirely compatible if transition from fcc- δ to fct- ϵ involves a continuous anisotropic expansion of the cubic phase, as reported by Vaughan and Bridge.⁵

Regarding the solubility coefficient (K_1), analysis of the function shows that it obeys an essentially parabolic relation, decreasing from a value of ~ 8.57 at $\text{ZrH}_{1.4}$, attaining a minimum of ~ 8.29 at $\text{ZrH}_{1.59}$, and then increasing at an increasing rate to ~ 9.55 at $\text{ZrH}_{1.9}$. The function is shown graphically in Figure 9. This behavior is not evident from the spacing of the isochores of Figure 7, and would not be anticipated from a plot that apparently involves continuously increasing spacing of $(\frac{1}{T})$ for equal increments of composition (X).

One may speculate that it is more than mere coincidence that the minimum occurs at the composition $\text{ZrH}_{1.59}$, approximating the δ , $\delta + \epsilon$ boundary, variously reported as $\text{ZrH}_{1.56}$ to $\text{ZrH}_{1.61}$.^{9,10,13} Undoubtedly, because of the related nature of this function and activity, significance must be afforded the fact that this is also the composition at which the most thermodynamically stable hydride in the binary occurs, as computed from activities by the method of Searcy and Meschi¹⁸ (See Figure 10). While a discontinuity in the plot of the activities of the metal and the gas does not exist at this composition, as would be a necessary requisite for a first-order transformation, we might well anticipate occurrence of a higher-order transformation, such as an ordering reaction or diffusionless shear mechanism, in solutions more concentrated than $\text{ZrH}_{1.6}$ (i.e., the $\delta \rightarrow \epsilon$ transformation). Maximums or inflections in the properties of hardness, strength, and resistivity have indeed been reported^{20,21} at ~ 61 at. % hydrogen, the approximate composition of this, the most thermodynamically stable hydride.

In view of (a) the results of this investigation, (b) the martensite-like nature of the $\delta \rightarrow \epsilon$ transformation, (c) the fact that the two phases (δ and ϵ) have not been observed to coexist at high temperatures, and (d) the effect of oxygen (and undoubtedly the other interstitial impurities, nitrogen and carbon) on the extent of the observed two-phase field, it is proposed that the $\delta \rightarrow \epsilon$

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Figure 10. Activities of Hydrogen and Zirconium in the Zr-H System at 600°C (Searcy and Meschi¹⁸)

transformation should appear on the binary phase diagram as a dotted line, denoting the ϵ -transformation start, extending upward from the composition $\text{ZrH}_{1.59}$, and probably bending toward the ZrH_2 axis at higher temperatures. The proposed $\delta \rightarrow \epsilon$ boundary is likened to the M_s line in an athermally activated martensite transformation, thermal fluctuations and excessive solute concentration serving as the driving force in the instance of "isothermal" transformation. The hydrogen-rich end of the binary phase diagram, including the proposed ϵ -start boundary, is shown in Figure 11. Curvature has been constructed in accordance with available data on the extent of the two-phase $\delta \rightarrow \delta + \epsilon$ boundary.

Based on this study, we may conclude that isochores of the δ - ϵ regions of the zirconium-hydrogen system must exhibit a progressively increasing change in spacing with increasing hydrogen concentration. Any deviation from this type of progression can be attributed to significant contamination of the binary with oxygen, nitrogen, etc., to form a ternary or higher-order alloy system.

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Figure 11. Proposed Phase Diagram of the Zirconium-Hydrogen System

V. CONCLUSIONS

Equilibrium dissociation pressures of the δ - and ϵ -phase regions in the zirconium-hydrogen binary can be expressed by a single equation involving pressure, temperature, and hydrogen-to-zirconium atom ratio. Examination of this expression permits the following conclusions:

- a) Equilibrium dissociation pressure of the δ and ϵ phases is a continuous function of hydrogen concentration, exhibiting no pressure discontinuities or anomalous isochore spacing over the H/Zr composition range of ~ 1.4 through 1.9.
- b) The partial molal heat of solution of hydrogen in the δ and ϵ hydride phases decreases continuously with increasing solute concentration at a decreasing rate, exhibiting no break or discontinuity at the $\delta \rightarrow \epsilon$ transformation composition. The quantity varies from -46.3 kcal/mole, for δ of composition H/Zr = 1.4, to -37.7 kcal/mole, for ϵ of composition H/Zr = 1.9.

Based on the results of this investigation, together with prior knowledge of the system (i.e., martensitic nature of the $\delta \rightarrow \epsilon$ transformation, absence of the two-phase region at higher temperatures, effect of interstitial impurities on the extent of the two-phase region, etc.), the phase diagram presented in Figure 11 is postulated. The dotted line, extending upward from the composition $\text{ZrH}_{1.59}$ and bending toward the ZrH_2 axis with increasing temperature, represents the " ϵ -start" boundary (i.e., the beginning of the cubic to tetragonal transformation). The extent and exact curvature of the boundary, while primarily speculative, has been constructed in accordance with reported δ - ϵ co-existence.

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