[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, ILLINOIS INSTITUTE OF TECHNOLOGY]

Solid Solution Equilibria in the Zirconium–Hydrogen System[1]

BY RUSSELL K. EDWARDS, P. LEVESQUE AND D. CUBICCIOTTI

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The solubility of hydrogen in zirconium and zirconium–hydrogen phases has been determined as a function of hydrogen pressure (range 1 to 760 mm. of Hg) and temperature (range 600 to 900°). The chemistry of the solid state is represented by a partial binary phase diagram showing extended solid solution ranges in four phases. Hydrogen will dissolve in the low temperature hexagonal close-packed α-form of zirconium to an extent which varies from 49.0 to 50.7 atom % hydrogen as the temperature is varied from 700 to 850°. The high temperature body-centered cubic β-form of zirconium will dissolve hydrogen to an extent which varies from 51.2 to 52.2 atom % hydrogen as the temperature is varied from 850 to 875°. Respective two-phase regions extend from the above composition limits to the composition limit of 59.4 atom % hydrogen which is invariant with temperature. A phase designated "δ" exists in the composition interval 59.4 to about 61 atom % hydrogen. A phase designated "ϵ" exists in the interval of about 62 atom % hydrogen to compositions approaching ZrH_2. The study is discussed in correlation with previous solubility, magnetic susceptibility, and X-ray diffraction investigations. We obtained no evidence of "definite" compounds of the formulas Zr_2H or ZrH reported by other workers.

Introduction

The phenomenon of extensive interaction of hydrogen with many of the transition metals to form products of metallic behavior affords a unique opportunity for study of special aspects of metallic bonding. That the molecularity of hydrogen is broken down as the gas enters the metal was first established by Hoitsema and later amply verified when it was shown that the initial hydrogen solubility was proportional to the square root of the hydrogen pressure.[2] Rundle, Shull and Wollan's[3] recent neutron diffraction studies on the high hydrogen composition phases ThH_2 and ZrH_2 have located the atomic sized particles in slightly flattened metallic tetrahedra. Coehn and co-workers demonstrated, moreover, that the particle in the case of palladium solutions supersaturated with hydrogen was the proton, as the dissolved hydrogen was found to migrate toward the cathode on passage of an electric current.[2] Wagner and Heller[4] have conclusively verified that transfer takes place also in normally saturated solutions. Palladium, thorium and zirconium lose their paramagnetism on solution of hydrogen by the time compositions $PdH_{0.66}$, ThH_2 and ZrH_2, respectively, are reached[2,3,5]; consequently the protonic nature of the hydrogen is supported. It seems both interesting and reasonable to assume the bonding in the metal–hydrogen solid solutions to be of the nature of the metallic bond itself, but to be exceptional due to the great size disparity between the atoms.

Several of the interpretations of physical measurements in the Zr–H system have been unsatisfactory because of the lack of knowledge of the phase equilibria behavior in the solid system. The present investigation was conducted for the purpose of determining the relevant binary phase diagram, with the objective of establishing suitable reference conditions for related studies being conducted in this Laboratory. The study was made by the method of measurement of the equilibrium hydrogen pressure in a series of isothermal observations as the composition of the solid was varied by successive additions of measured volumes of hydrogen. Preliminary measurements had indicated some 10% discrepancy from the work of Hall, Martin and Rees,[6] who carried out a similar investigation. Related measurements at very low hydrogen compositions have been reported by de Boer and Fast,[7] and very recently by Schwartz and Mallett.[8]

Experimental

Apparatus.—The vacuum line used in the experimental work was pumped by a system consisting of a mechanical pump, a two-stage mercury diffusion pump, and a Dry Ice–chloroform–acetone trap for condensable gases. Vacuum pressures were measured by means of an ionization gage isolated from mercury vapor and other condensable gases by a liquid nitrogen trap.

The hydrogen purification train consisted, in the following order, of (1) a furnace-heated quartz glass tube filled with 5% platinized asbestos and operated at 225°; (2) a ten-inch spiral trap at liquid nitrogen temperature; and (3) a furnace-heated quartz glass tube filled with fine zirconium metal turnings and held during operation at a temperature of 800°. A 100-ml. water-jacketed gas buret was used in conjunction with a mercury leveling bulb for gas volume measurements. The buret was graduated to 0.2 ml. and readings were estimated to 0.05 ml. The position of a leveling bulb was controlled by a counterbalance weight and pulley arrangement. Volume measurements were made at atmospheric pressures as determined by a null reading on an open-arm mercury manometer. Atmospheric pressure measurements were read on an external laboratory mercury manometer. A thermometer graduated to 0.1 ml. was in the water jacket of the buret and another similar thermometer was taped to the glass tubing in a position to register any temperature fluctuation in the gas volume region not within the buret. The temperature of the gas volume system was held constant during measurements to ±0.1° by use of a combination heater–cooler air circulating fan.

The reaction chamber was an 8-mm. quartz glass tube and the sample inside was additionally contained in a small alumina thimble. The sample was introduced at the Pyrex end (a graded seal connected this to the quartz glass section)

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[2] For a review of the very extensive literature on the subject and an essentially complete bibliography up to 1947, see D. P. Smith, "Hydrogen in Metals," The University of Chicago Press, Chicago, 1948.

[3] R. E. Rundle, C. G. Shull and E. O. Wollan, *Acta Cryst.*, **5**, 22 (1952).

[4] C. Wagner and G. Heller, *Z. physik. Chem.*, **B46**, 242 (1940).

[5] J. Fitzwilliam, A. Kaufmann and C. Squire, *J. Chem. Phys.*, **9**, 678 (1941).

[6] M. N. A. Hall, S. L. H. Martin and A. L. G. Rees, *Trans. Faraday Soc.*, **41**, 306 (1945).

[7] J. H. de Boer and J. D. Fast, *Rec. trav. chim.*, **55**, 350 (1936).

[8] C. M. Schwartz and M. W. Mallett, *Trans. Amer. Soc. Metals*, **46**, 640 (1954).

and slid down into an alumina boat when the quartz glass tube was tipped downward. The tube was then sealed and returned to the horizontal position. The tipping operation was accomplished as the appropriate glass section was worked at suitable temperature. A calibrated chromel-alumel thermocouple was placed outside the quartz tube with its junction directly beside the specimen. A porcelain tube was then placed around the assembly and fitted through a firebrick into a resistance furnace. A Leeds and Northrup Micromax recorder-controller, acting on the signal from a thermocouple near the furnace windings, served to regulate the furnace temperature within such a tolerance that the sample zone itself could be held to ±1°. A Rubicon precision potentiometer was used to measure the millivoltage of the sample zone thermocouple. The major portion of the apparatus was shielded from furnace heat by a framework of aluminum foil-lined asbestos panels. The furnace was mounted on wheels which ran along tracks and safe movement back and forth to a reproducible operating position was achieved simply.

The equilibrium hydrogen gas pressures over the sample were read on a mercury manometer. Pressures were estimated to ±0.5 mm.

Materials.—The zirconium was in the form of wire of 0.015 inch diameter and was obtained from the Foote Mineral Company. The analysis supplied with the material was 2.5–3.0% Hf, 0.04% Fe, 0.03% O, and 0.01% N.

Commercial hydrogen was purified by passing it over shredded 5% platinized asbestos heated to 225° and then through the trap section at liquid nitrogen temperature to remove all traces of water. Finally the hydrogen was passed through zirconium turnings at 800° to "getter" impurities such as nitrogen, carbon dioxide or any remaining oxygen or water vapor. The turnings, on cooling in the hydrogen atmosphere, would take up a considerable quantity of hydrogen which could later be liberated for experimental use as desired on reheating the turnings. In some cases the gas was used directly as it passed slowly through the purification train.

Procedure.—About 50 mg. of zirconium wire was used in a typical determination of a pressure–composition isotherm. The wire was cleaned by abrasion with 2/0 emery paper, weighed and introduced into the apparatus. The system was evacuated for at least 18 hours and to a pressure of less than 10^{-5} mm. Then hydrogen was flushed through the system twice, following which the sample was brought rapidly to the desired temperature in the presence of hydrogen, at a pressure of about 300 mm. The system was next evacuated for fifteen minutes to free the sample of hydrogen, and the determination of an isotherm was commenced. The rate of absorption of the hydrogen nearly always was very fast. In any case in which this was not so, the run was discontinued and a new sample was introduced. As a standard procedure, after each successive addition of hydrogen the equilibrium was considered to prevail if no more than 0.5 mm. of change in pressure occurred within ten minutes. Check observations over longer periods of time showed this practice to be reliable.

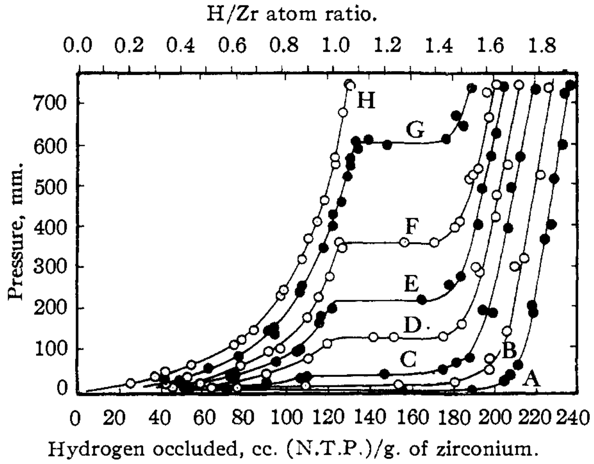

Fig. 1.—Isothermal pressure–volume curves for the temperature range 600 to 900°: A, 600°; B, 700°; C, 750°; D, 800°; E, 825°; F, 850°; G, 875°; H, 900°.

The hydrogen pressures recorded by means of the adopted standard procedure are assumed to be representative of equilibrium conditions; the same hydrogen pressure was recorded for a solid of a given composition whether that composition was reached by addition of hydrogen to a solid of lesser hydrogen content or by subtraction of hydrogen from a solid of greater hydrogen content. That no systematic irreversible side reactions were important will be apparent from consideration of the isotherm obtained for the temperature 875°. This isotherm is based on five independent experimental runs on a single Zr specimen. Each run traversed the entire composition range, and between runs the hydrogen was completely removed by evacuation of the apparatus while holding the sample at a temperature in excess of 825° for not less than thirty minutes. The data for all five runs fit the given isotherm within the estimated experimental error.

X-Ray diffraction patterns were taken on both the original wires and the residual specimen wires after they had been fully saturated with hydrogen at a given temperature and under a hydrogen pressure of one atmosphere, and additionally cooled in the presence of hydrogen at one atmosphere pressure.

The measurements are estimated to be precise to within ±1.0 mm. in the pressure, ±1.0° in the temperature, and ±1.5 ml. of hydrogen per gram of zirconium in the composition. The measurement of the diminution of the hydrogen volume as registered by the gas buret was used in the calculation of the compositions of the solid solutions. Correction of the composition for the amount of hydrogen remaining in the reaction zone gas phase was accomplished through comparison with a complete series of blank determinations made in the absence of a sample and at all temperatures and pressures.

Metallic impurities have been included in the composition calculations as zirconium. The principal impurity, hafnium, is known[9] to behave much like zirconium with respect to hydrogen occlusion.

Hydrogen gas volumes at "N.T.P." refer to calculated volumes at 0° and at one atmosphere pressure.

Results

Some experimental pressure–composition isotherms are shown in Fig. 1 with the estimated determinant experimental error represented by the size of the data points. In general each isotherm given is based on the data of two independent experimental runs, using two different zirconium samples. However, the 850° isotherm was based on three independent runs on three independent samples whereas the 875° isotherm was based on five independent runs on only one sample. Figure 2 shows similar isotherms at the additional temperatures 885, 865, 860 and 855°, the last three of which were supplementally determined with special emphasis on searching for the α-β zirconium transformation, as will be apparent later in the discussion.

Estimation of the compositions at the phase field boundaries was accomplished by plotting the logarithm of hydrogen pressure *versus* the logarithm of hydrogen composition in atom % and extrapolating the curves to intersection. The log–log form of plotting improves the linearity, presumably by smoothing simple power or exponential dependencies, so that more consistent extrapolation to phase field boundaries is possible. In particular, highly linear plots result in the region of the boundary between the $(\alpha + \delta)$ and δ-phase fields. For this boundary a composition of 59.4 ± 1.0 atom % hydrogen is found, and this value seems invariant with temperature within the experimental error.

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(9) S. S. Sidhu and J. C. McGuire, *J. App. Phys.*, **23**, 1257 (1952).

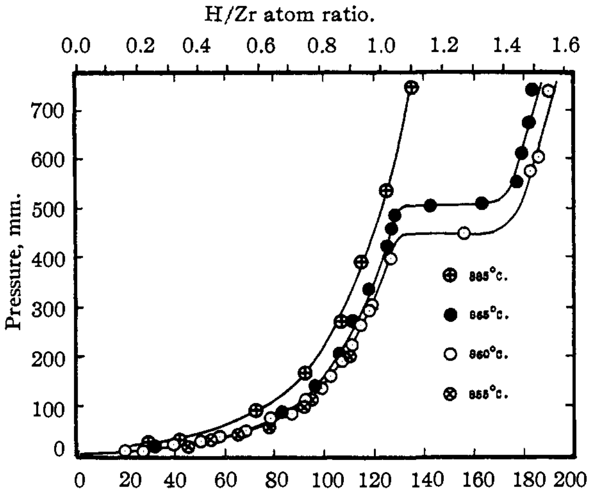

Fig. 2.—Isothermal pressure–volume curves for the temperature range 855 to 865°.

The phase field boundary composition data are listed in Table I and are plotted *versus* temperature in the partial phase diagram shown in Fig. 3.

TABLE I

EXPERIMENTAL COMPOSITION LIMITS IN THE Zr–H SYSTEM (IN ATOM % HYDROGEN)

Temp., °C.	Two-phase field	Isobaric limit for 760 mm.
	($\alpha + \delta$)	
600	.. to ..	65.9
700	49.0 to 59.6	65.1
750	49.6 to 58.9	64.2
800	50.1 to 59.6	63.4
825	50.4 to 59.4	62.8
850	50.7 to 59.3	62.2
	($\beta + \delta$)	
850	51.5 to 59.3	62.2
860	51.9 to 59.3	61.2
875	52.2 to 59.3	60.7
885	.. to ..	52.6
900	.. to ..	51.6

Table II lists pressure–temperature data for some pertinent compositions, taken from the smoothed pressure–composition isotherms. These data were plotted in the conventional manner—logarithm of pressure *versus* reciprocal absolute temperature—and the derived partial molal heat of solution data for molecular hydrogen gas dissolving in Zr–H solid solutions have been listed in Table III, together with the corresponding partial molal entropy of solution data. Evaluation of thermodynamic quantities for the composition 63.1 atom % hydrogen was too questionable to record. Applicability of the data listed for the composition 62.0 atom % hydrogen above the temperature 750° is also to be questioned.

TABLE II

EQUILIBRIUM H_2 PRESSURES IN MM. *versus* TEMPERATURE AT VARIOUS Zr–H COMPOSITIONS

Temp., °C.	Composition, atom % hydrogen 39.4	42.3	44.9	47.2	55.0	60.7	62.0	63.1
600	...	...	...	..	..	5	12	54
700	4	5.5	7.5	11	12	36	77	247
750	10.5	15	21	30	40	98	245	500
800	27	35	51	76	127	225	450	695
825	42	55	78	120	220	378	620	..
850	60	83	123	174	360	520	737	..
860	73	100	145	212	450	675	..	..
865	80	110	158	242	507	..	..	..
875	92	128	184	263	608	760	..	..
900	130	180	252	355	..	..	..	..

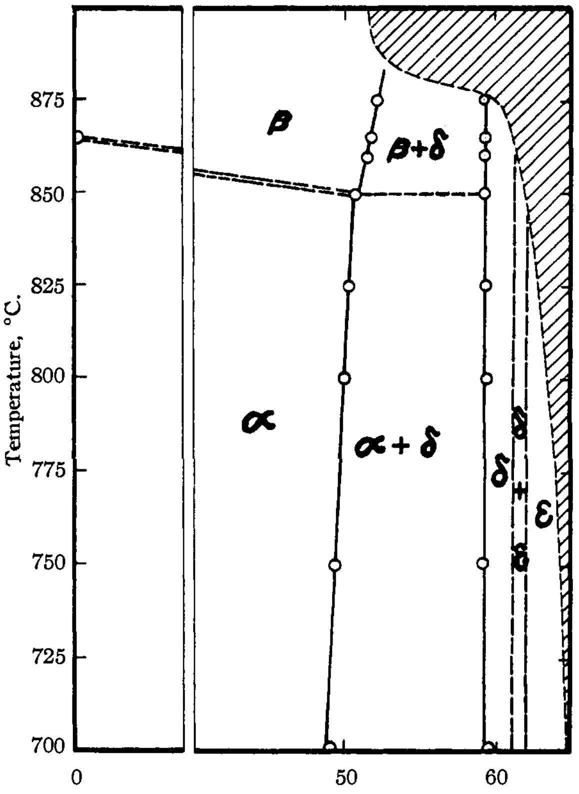

Fig. 3.—Partial phase diagram of the zirconium–hydrogen system for the condensed phases. (Shaded area denotes region for which hydrogen pressures are in excess of one atmosphere. Measurements were not carried out in this region.)

TABLE III

PARTIAL MOLAL HEATS AND ENTROPIES OF SOLUTION OF H_2 IN Zr–H SOLID SOLUTIONS

Composition, atom % hydrogen	$\overline{\Delta H^0}$, kcal./mole	$\overline{\Delta S^0}$, cal./mole/deg.
39.4	−39.6	−30.2
42.3	−39.6	−30.9
44.9	−39.6	−31.6
47.2	−39.6	−32.3
55.0	−49.6	−42.7
60.7	−39.6	−34.6
62.0	−39.6	−36.4

Discussion

The partial phase diagram shown in Fig. 3 has been induced for the temperature interval between 700 and 900°. The symbols for identification of phases have been selected with as logical a correspondence as possible to those used by Hägg[10] in his X-ray studies. Hägg's conclusions have been criticized by Smith.[2] It is to be borne in mind that all of the X-ray studies were conducted at room temperature, several hundred degrees lower than the present work.

The low temperature allotrope of Zr has been customarily designated as the α-modification. It transforms at 865° from its hexagonal close-packed symmetry to a phase designated as the β-modification with body-centered cubic symmetry. In the binary diagram we have similarly labeled what we believe to be the corresponding primary solid solution fields in the Zr-rich regions. The ϵ-phase, which approaches the composition corresponding with ZrH_2 at the highest hydrogen compositions, was reported to be face-centered tetragonal by Hägg. Rundle, Shull and Wollan[3] interpreted their X-ray and neutron diffraction results on this phase to indicate that it was body-centered tetragonal, but they established through equivalence of interplanar distances that they were dealing with the same phase as that designated ϵ by Hägg. Our X-ray diffraction measurements established clearly the equivalence of our ϵ-phase and that of Hägg. We have no evidence of the existence of the phase at Zr_2H which Hägg designated γ, but Jack[11] has recently indicated that he has encountered a face-centered tetragonal phase of such a composition in the case of 300° preparations cooled rapidly to room temperature. Annealing at 300° seemed to cause the disappearance of the phase.

We obtained no direct evidence in this binary study as to the existence of the phase we have designated δ. However, Edwards and Levesque[12] have subsequently conducted an investigation of the ternary Zr–O–H system and have clearly encountered a reasonably wide $(\delta + \epsilon)$ two-phase region, which becomes increasingly narrow as the composition approaches that of the binary system. From the nature of their ternary diagram it is apparent that the $(\delta + \epsilon)$ two-phase field must exist in the binary system, and their extrapolation to the binary system leads to estimated two-phase compositions of a range of about 61 to 62 atom % hydrogen at 750°, but the composition range could easily be more narrow. Such a very narrow isothermal invariant region would not be detected in our binary measurements. Their data indicate that the region probably extends to at least as high a temperature as 850°. In the ternary system their data indicate a joining of the $(\alpha + \delta)$ and $(\delta + \epsilon)$ regions at temperatures of about 860°. The present investigation places the zirconium-rich boundary of the δ-phase at 59.4 ± 1.0 atom % hydrogen and indicates this boundary is invariant with temperature. The high-hydrogen composition boundary is probably at about 61 atom % hydrogen, based on the work of Edwards and Levesque.[12]

We have used the designation, δ, on the supposition that the phase should probably be identified with Hägg's δ-phase of face-centered cubic symmetry, which was presumed however to correspond to a composition of approximately ZrH. We have done so in view of analogy based on the work of Sidhu and McGuire[9] who found a face-centered cubic phase in the hafnium–hydrogen system in the single phase composition region 63.0 to 64.8 atom % hydrogen. It is seen from Fig. 3 that extrapolation of the $(\alpha + \delta)$ two-phase field boundaries to the temperature of Hägg's X-ray studies would indicate that his presumed approximately ZrH compound would lie well out in the $(\alpha + \delta)$ two-phase field so he would have observed some of the δ-phase. In fact, if linear extrapolation of the two-phase boundaries to the lower temperatures could be assumed reasonable, it would lead to an estimation that about 40% of the two-phase mixture would be the δ-phase at a composition nominally corresponding to ZrH.

The $(\alpha + \beta)$ two-phase region was drawn in on the basis of the knowledge of the α–β transformation temperature for the pure metal and the character of the join of the zirconium-rich boundary of the $(\beta + \delta)$ and $(\alpha + \delta)$ regions. Special supplementary runs were carried out in the temperature interval between 850 and 875° with composition changes being conducted in small steps with a view to finding the invariant isothermal pressure region corresponding to the α–β transformation. Within our experimental error, we were unable to observe the anticipated behavior and we conclude that the $(\alpha + \beta)$ field is probably very narrow in the direction of the temperature ordinate and that the α–β transformation takes place in the very limited temperature interval between 865 and 850° or less.

That the transformation temperature is lowered initially on addition of hydrogen was well established by de Boer and Fast[7] in their low pressure–low hydrogen composition studies. The conclusion of Fitzwilliam, Kaufman and Squire[5] that uptake of hydrogen by zirconium lowers the α–β transformation temperature by as much as 200° was based on the observation of the magnetic susceptibility as a function of temperature of a sample being heated in hydrogen at one atmosphere pressure. They noted that at about 700° the magnetic susceptibility increased rapidly with temperature in a manner analogous with the behavior for the pure metal at the α–β transition temperature, and that the hydrogen uptake began slowly. However, they were surprised to find the susceptibility to fall off rapidly with temperature thereafter, whereas the magnetic susceptibility of the pure metal had remained nearly constant with temperature after the α–β transition. It is easy to see why the falling off in the case of the metal with hydrogen since the composition would be changing due to the taking up of hydrogen, and transformation toward the ϵ-phase would be under way.

The considerable, apparent lowering of the α–β transformation temperature is not in accord with the interpretation of the present work and considerably weakens our case for assuming the α–β–δ eutectoid join to be in the temperature region 850 to 860°. Those authors did not list any composition data for the measurements just mentioned, but one would assume that the presumed transforma-

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(10) G. Hägg, *Z. physik. Chem.*, **11B**, 433 (1931).

(11) K. H. Jack, private discussion, Illinois Institute of Technology, July 28, 1953.

(12) Russell K. Edwards and Pascal Levesque, THIS JOURNAL, **77**, 1312 (1955).

tion took place at very low hydrogen content. If this were true, then the ($\alpha + \beta$) region should be shown dropping precipitously in our diagram. Our work requires that the region either be close in composition to the pure metal (in which case we could not have detected it in our isotherms since pressures would have been too low) or too narrow to detect on our isotherms.

In this connection it is of interest to consider the recent study by Schwartz and Mallett.[8] X-Ray and electron diffraction analyses gave patterns corresponding to those given by Hägg for the δ- and ϵ-phases, but an additional "tetragonal (pseudocubic)" phase of unidentified composition was encountered. Their evidence favors the latter phase as the one which coexists in equilibrium with metallic zirconium. Their metallographic data indicate that only a very small amount of hydrogen may be dissolved in zirconium before this pseudocubic phase makes its appearance. It is well to point out again that the diffraction and metallographic observations were made at room temperature whereas the magnetic susceptibility measurements and the isothermal equilibrium pressure measurements of our study were made at high temperatures.

One aspect of the work of Fitzwilliam, Kaufmann and Squire[5] is in agreement with predictions one would make, assuming the correctness of our diagram. Their three room temperature magnetic susceptibility measurements for compositions intermediate between Zr and ZrH_2 are linear with composition within experimental error, although these authors did not comment on this point. The compositions of the material on which measurements were made lie very close to those which we would give for the ($\alpha + \delta$) region plus part of the narrow δ-region, at room temperature, and linearity would of course be expected throughout the two-phase region.

The thermodynamic data listed in Table III can now be discussed as to significance by referring to the phase diagram given in Fig. 3. Since the composition of the ($\alpha + \delta$)–δ boundary is invariant with temperature, the $\overline{\Delta H^0}$ and $\overline{\Delta S^0}$ values listed for the composition 55.0 atom % hydrogen, which falls in the two-phase region, can be taken as belonging to the δ-phase along its zirconium-rich boundary. The value of $\overline{\Delta H^0} = -39.6$ kcal. per mole of molecular hydrogen for the α-phase appears not to vary with composition, and if this value is assumed to be valid along the α–($\alpha + \delta$) boundary, calculation of the $\overline{\Delta S^0}$ for various compositions along the boundary becomes possible since the α- and δ-phases are in equilibrium. The α–($\alpha + \delta$) boundary composition of 50 atom % hydrogen occurs at about 1057°K. and a value of $\overline{\Delta S^0} = -33.2$ cal./mole/deg. for the solution of molecular hydrogen in the α-phase is obtained at this composition. The entropy of the gas at that temperature is 40.10 cal./mole/deg., and if this value is added to the value above and the result divided by two, a value of $\overline{S^0} =$ 3.5 entropy units per gram atom is obtained for the partial molal entropy of monatomic hydrogen in this particular solid solution in zirconium metal. For the δ-phase a value of $\overline{S^0} = -1.3$ entropy units per gram atom hydrogen is obtained. A value of $\overline{\Delta H^0} = -5.0$ kcal. per gram atom hydrogen is obtained for the partial molal heat of transfer of hydrogen from the α-phase to the δ-phase for the case of the two phases in equilibrium.

It does not seem advisable at this time to assign significance to the heat and entropy data obtained for the compositions 60.7 and 62.0 atom % hydrogen in view of the fact that within the experimental error the values cannot be clearly associated with either single-phase regions or two-phase regions. Moreover, the nature of the temperature variation of the composition of the boundaries of the ($\delta + \epsilon$) phase field is quite uncertain.

Hildebrand and Scott[13] have discussed intermetallic solid solutions in an extension of their treatment of solution theory. They have tabulated solubility parameters and have listed a value of 94 units for zirconium metal.

We have used the results of the cohesive energy and density calculations of Wigner and Huntington[14] to calculate a solubility parameter of 79 units for "metallic hydrogen." We have also used the above cohesive energy in conjunction with the metallic radius for hydrogen given by Pauling and Ewing,[15] which was found to be consistent with more recent work,[3] and have obtained a solubility parameter of 117 units. The mean value, 98 units, might be selected as representative for metallic hydrogen. The proximity of this value to the parameters for the refractory metals is surprising and taken alone would lead to the prediction of wide solid solubility in the zirconium–hydrogen system.

It is to be recognized that the diagram presented may well be incomplete in that the method of measurement is unsatisfactory for detection of very narrow two-phase fields or those occurring at very low pressures unless a more sensitive gas pressure and volume measuring apparatus is used. However, we believe that the diagram presented here should provide a somewhat sounder basis for future investigations relating to solid state phenomena in the system.

The values which we obtained for the total uptake of hydrogen by zirconium for a given pressure of one atmosphere were about 10% higher than those given by Hall, Martin and Rees.[6]

CHICAGO, ILLINOIS

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(13) J. H. Hildebrand and R. L. Scott, "The Solubility of Nonelectrolytes," Reinhold Publ. Corp., New York, N. Y., 1950.

(14) E. Wigner and H. B. Huntington, *J. Chem. Phys.*, **3**, 764 (1935).

(15) L. Pauling and F. J. Ewing, THIS JOURNAL, **70**, 1660 (1948).