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

Solid Solution Equilibria in the Ternary System Zirconium-Oxygen-Hydrogen[1]

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RECEIVED APRIL 9, 1954

The solubility of hydrogen in the solid solutions of the ternary zirconium-oxygen-hydrogen system has been determined as a function of temperature (range 600 to 900°), composition and equilibrium hydrogen pressure. The data have been correlated with those of the related binary systems and some previous work in the ternary system to yield an extensive provisional partial ternary phase diagram. An isothermal section of the diagram at 750° may be used to describe the solid state chemistry of the system. The α-, δ- and ϵ-phases show extensive solid solubility of both hydrogen and oxygen simultaneously. At 750° the hydrogen saturation boundary of the α-Zr phase shows that initially hydrogen may be replaced by oxygen on a three-to-one basis in the α-phase. The hydrogen saturation boundary of the δ-phase indicates that hydrogen may be replaced by oxygen on a seven-to-two basis in the δ-phase. Extrapolation of the composition boundaries of the δ-phase field leads to boundary compositions of about 61 and 62 atom % hydrogen for the δ-phase in the binary zirconium-hydrogen system. Chemical interaction of the interstitial hydrogen and oxygen within the α-zirconium metallic lattice is not apparent.

Introduction

The solid solubility of oxygen in zirconium metal has long been considered to be very high.[2,3] A recent thorough phase diagram study in the zirconium-oxygen system by Domagala and McPherson[4] has set the solubility at 29 atom % oxygen in the temperature range 600 to 900°. Edwards, Levesque and Cubicciotti[5] presented a partial phase diagram for the zirconium-hydrogen system and have indicated a primary solid solubility for hydrogen in zirconium of from 49 atom % at 700° to 52 atom % at 875°. Hall, Martin and Rees,[6] who studied the effect of oxygen on the solubility of hydrogen in zirconium-oxygen solid solutions, observed that apparently the "volume of hydrogen sorbed at saturation decreased by a volume equivalent to that of oxygen present." This observation has been considered of notable interest by Smith,[7] who presumably was concerned with the implications of such behavior with regard to his rift theory as the mode of occlusion of hydrogen in metals.

It occurred to us that the observed "equivalence" might be readily explained if one assumed that the addition of oxygen brought about the conversion of ZrH_2 to ZrO_2 since these are the saturation phases with respect to the two components, hydrogen and oxygen.

On the other hand the wide solid solubility, discussed above, of hydrogen and oxygen in zirconium would lead to a prediction of extensive ternary solubility. One might envisage this ternary solution as a metallic zirconium matrix lattice with the interstices variously filled with the small hydrogen and oxygen particles. The idealized hexagonal close-packed lattice can provide both octahedral and tetrahedral interstices. De Boer and Fast[8] have shown by several experiments that oxygen in zirconium migrates as a negatively charged particle on passage of an electrical current. In contrast to this behavior, the work of Coehn and coworkers, and also of Wagner and Heller, showed hydrogen in palladium solid solutions to migrate with passage of an electrical current as though it were positively charged.[5] We might expect some rather striking manifestations of interaction on partial replacement of hydrogen by oxygen within the interstices, particularly in view of the conspicuous differences in both sizes and electron affinities.

The present investigation was conducted by the method of measuring the equilibrium hydrogen pressure over ternary solid solutions as a function of composition and temperature. The composition was varied by successive additions of measured volumes of hydrogen to an initially homogeneous oxygen-zirconium solid solution in which the composition ratio of zirconium to oxygen remained constant.

Experimental

Each zirconium-oxygen solid solution specimen was prepared by controlled oxidation of about 100 mg. of 0.015-inch diameter zirconium wire, followed by equilibration of the resulting metal and oxide mixture for 20 minutes *in vacuo* at a temperature approximately 200° below the melting point of the particular composition. Equilibration heating was by electrical resistance heating of the wire *in vacuo*. The procedure has been previously described.[3] The homogeneous nature of each preparation was carefully established by X-ray diffraction examination before it was considered a suitable specimen for study. After the composition was established by weight difference on oxygen uptake as observed on an Ainsworth semi-micro balance, a middle section of the wire was cut out for use in the hydrogen solubility determination.

Numerous preliminary attempts at equilibration by holding a preparation at 1200° for 12 hours did not always result in a homogeneous single phase solution, and the procedure was abandoned as unreliable. Hall, Martin and Rees reported the latter procedure to be satisfactory at 950° in their work.[6]

Materials.—Zirconium wire of 0.015-inch diameter obtained from the Foote Mineral Company was used. The analysis has been given previously.[5] Commercial 99.8% pure tank oxygen was used without additional purification.

Procedure.—The apparatus and procedure for determining the equilibrium hydrogen pressure as a function of temperature and composition of the ternary material were those earlier used in the binary zirconium-hydrogen study, and

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[1] (a) Presented before the Division of Physical and Inorganic Chemistry, 125th National American Chemical Society meeting, March, 1954. (b) This work was carried out under the sponsorship of the United States Office of Naval Research. Complete details and data have been given in Technical Report No. 14, Chemical Thermodynamics of Materials at High Temperatures, U. S. Navy, Office of Naval Research, Contract N7-onr-329, Task Order II, Project No. 358-070, August, 1953. (c) Based on part of a thesis submitted by Pascal Levesque to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1953.

[2] J. H. de Boer and J. D. Fast, *Rec. trav. chim.*, **55**, 459 (1936).

[3] D. Cubicciotti, THIS JOURNAL, **73**, 2032 (1951).

[4] R. F. Domagala and D. J. McPherson, *Trans. Amer. Inst. Met. Eng.*, **200**, 238 (1954).

[5] R. K. Edwards, P. Levesque and D. Cubicciotti, THIS JOURNAL, **77**, 1307 (1955).

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

[7] D. P. Smith, "Hydrogen in Metals," The University of Chicago Press, Chicago, 1948.

[8] J. H. de Boer and J. D. Fast, *Rec. trav. chim.*, **59**, 161 (1940).

the same limits of error are assumed.[5] Families of isotherms were determined for samples of initial oxygen compositions of 6.3, 10.8, 18.6, 24.7 and 29.6 atom % in zirconium, and these values correspond to atom ratios, R, of oxygen in zirconium of 0.068, 0.121, 0.229, 0.328 and 0.420, respectively.

The criteria employed to ensure that measurements were made under true equilibrium conditions were the same as discussed previously with respect to the zirconium–hydrogen system.[5] The data for the 800° isotherm shown in Fig. 1 are from five independent experimental runs on a single zirconium–oxygen specimen. Each run traversed the entire composition range with respect to hydrogen, and between runs the hydrogen was completely removed in the manner described previously.[5] The data from all of the runs fit with equal precision the 800° isotherm given.

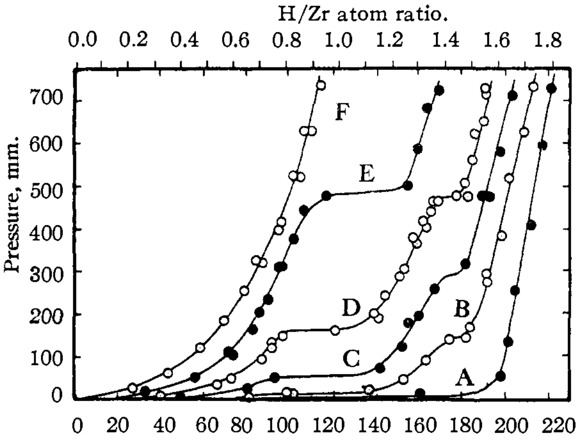

Fig. 1.—Isothermal pressure–volume curves for an alloy containing initially 6.3 atom % oxygen in the temperature range 600 to 900° (R = 0.068): A, 600°; B, 700°; C, 750°; D, 800°; E, 850°; F, 900°.

Results

The experimental data are shown in Figs. 1, 2, 3, 4 and 5, in which are given families of isotherms of equilibrium hydrogen pressure as a function of the volume[9] of hydrogen gas taken up per gram of zirconium metal in a sample of given R value.[10] Additional plots (not shown here) were made of the logarithm of hydrogen pressure *versus* the logarithm of atom % hydrogen composition. Advantage was taken of the reasonably linear nature of the extrapolations in the logarithmic plots to obtain the phase field boundary compositions listed in Table I. In Figs. 1 and 2 the unmistakable appearance of a second composition region of pressure arrest is apparent in addition to the one corresponding to the arrest in the binary system.[5] As noted above, the data shown on the 800° isotherm in Fig. 1 are the results of five different determinations and amply establish the existence of the second arrest as well as indicate something of the reproducibility of the data.

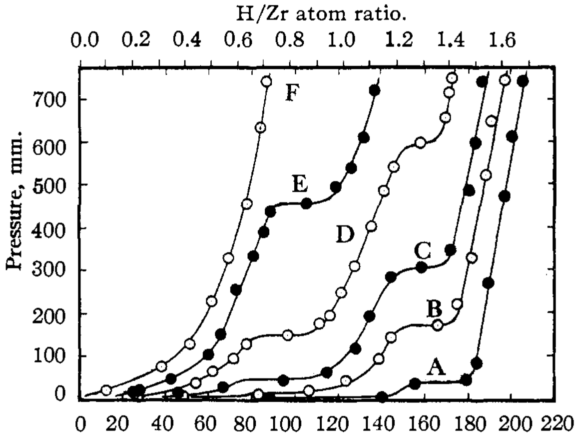

Fig. 2.—Isothermal pressure–volume curves for an alloy containing initially 10.8 atom % oxygen in the temperature range 600 to 900° (R = 0.121): A, 600°; B, 700°; C, 750°; D, 800°; E, 850°; F, 900°.

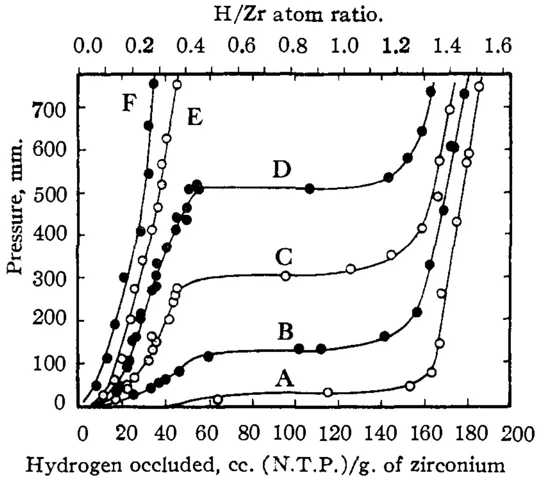

Fig. 3.—Isothermal pressure–volume curves for an alloy containing initially 18.6 atom % oxygen in the temperature range 600 to 900° (R = 0.229): A, 600°; B, 700°; C, 750°; D, 800°; E, 850°; F, 900°.

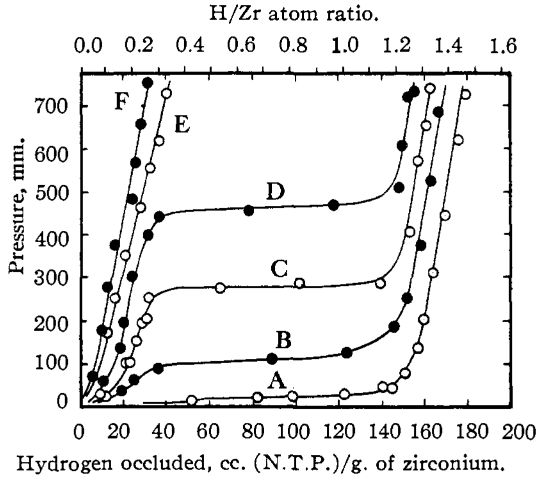

Fig. 4.—Isothermal pressure–volume curves for an alloy containing initially 24.7 atom % oxygen in the temperature range 600 to 900° (R = 0.328): A, 600°; B, 700°; C, 750°; D, 800°; E, 850°; F, 900°.

On the other hand, Figs. 3, 4 and 5 show only wide composition ranges of a single pressure arrest.

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[9] Volumes of hydrogen N.T.P. refer to the gas volume corrected to 0° and at a pressure of one atmosphere.

[10] Impurities (principally hafnium) were included as zirconium in the composition calculations.

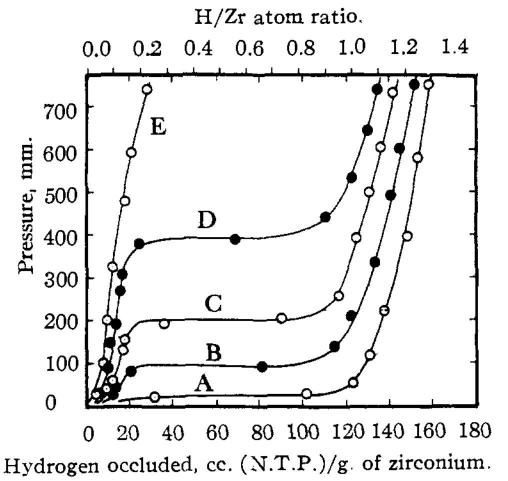

Fig. 5.—Isothermal pressure–volume curves for an alloy containing initially 29.6 atom % oxygen in the temperature range 600 to 850° (R = 0.420): A, 600°; B, 700°; C, 750°; D, 800°; E, 850°.

TABLE I

BOUNDARY COMPOSITIONS OF SOLID TWO-PHASE FIELDS IN THE Zr–O–H SYSTEM (COMPOSITIONS IN ATOM % HYDROGEN)

		Temperatures, °C.				
R	Boundary	600	700	750	800	850
0.068	$\alpha - (\alpha + \delta)$	..	..	42.8	42.9	45.7
	$(\alpha + \delta) - \delta$	..	50.1	51.2	51.2	53.7
	$\delta - (\delta + \epsilon)$	..	56.6	56.2	55.6	..
	$(\delta + \epsilon) - \epsilon$	..	58.0	58.0	58.0	..
0.121	$\alpha - (\alpha + \delta)$	..	34.8	35.9	36.7	39.1
	$(\alpha + \delta) - \delta$	..	42.7	43.4	44.2	47.0
	$\delta - (\delta + \epsilon)$	51.9	51.9	51.8	51.5	..
	$(\delta + \epsilon) - \epsilon$	55.6	55.3	55.0	54.3	..
0.229	$\alpha - (\alpha + \epsilon)$	..	25.7	25.3	25.0	..
	$(\alpha + \epsilon) - \epsilon$	49.0	48.4	49.6	49.6	..
0.328	$\alpha - (\alpha + \epsilon)$	..	15.0	17.1	17.1	..
	$(\alpha + \epsilon) - \epsilon$	45.2	45.7	46.8	47.3	..
0.420	$\alpha - (\alpha + \epsilon)$	..	9.6	12.0	12.0	..
	$(\alpha + \epsilon) - \epsilon$	38.9	38.9	38.9	39.3	..

Values of equilibrium hydrogen pressure as a function of temperature at several significant fixed compositions have been taken from the smoothed curves of Figs. 1, 2, 3, 4 and 5 and the data are tabulated in Table II. These data were used in plotting the logarithm of the hydrogen pressure *versus* the reciprocal temperature to obtain partial molal heats of solution of molecular hydrogen in the ternary solid solutions. These latter values are also given in Table II together with the corresponding partial molal entropies. Some of the derived values have been omitted because of questionable variation in the slopes of the plots.

A summarizing correlation is given in Fig. 6 where an isothermal section of a provisional ternary phase diagram is shown in part. The data for the binary zirconium–hydrogen system boundaries were taken from the work of Edwards, Levesque and Cubicciotti.[5] The data for the binary zirconium–oxygen system boundaries were taken from Domagala and McPherson.[4] The data of the composition region of R value greater than 0.420 we have obtained from replotting the data of the isotherms of Hall, Martin and Rees,[6] in the manner of the handling of our own data.

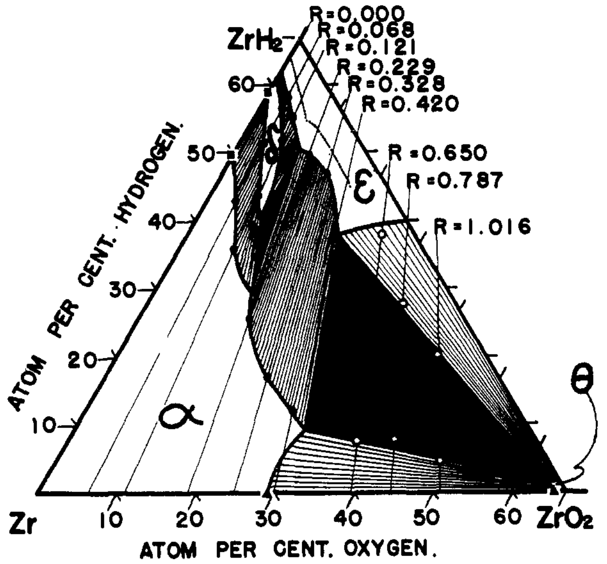

Fig. 6.—Ternary system Zr–O–H; provisional diagram for the condensed phases; isothermal cross-section at 750°. Two-phase regions are shaded by lines approximating tie-lines. Three-phase regions are drawn in solid black. Extension of boundaries beyond experimental data is by inference and therefore must be considered provisional. The lines across the diagram leading to R values represent experimental composition traverses as hydrogen was successively added to Zr–O solid solution specimens of constant O/Zr atom ratios, R. Dotted line represents a contour of the variation in composition at constant hydrogen pressure of 760 mm.: ●, this investigation; ○, Hall, Martin and Rees; ▲, Domagala and McPherson; ■, Edwards, Levesque and Cubicciotti.

Discussion

The solid state chemistry of the zirconium–oxygen–hydrogen system at the temperature 750° and at hydrogen pressures of less than 760 mm. can be shown by a quasi-ternary phase diagram of Zr–ZrO_2–ZrH_2 as is presented in Fig. 6. It is to be borne in mind that actually somewhat less than the hydrogen composition corresponding to ZrH_2 is reached under the given temperature and pressure conditions.[5] Nomenclature of phase fields is that previously adopted.[5]

A three-component system in the presence always of a gas phase will yield invariant isothermal pressure behavior with changing composition if three solid phases are present. In the following discussion the presence of a gas phase is to be understood and only the solid phases are explicitly discussed. The two-phase regions, however, may appear to show equivalent behavior if the change in composition happens to be effected along a tie-line connecting phase compositions of equal fugacity. As compositions are continuously and isothermally changed along a path traversing first a single phase, second a two-phase, and third a three-phase region, one would expect the following general behavior. The pressure isotherm would

TABLE II

EQUILIBRIUM PRESSURES AND PARTIAL MOLAL HEATS AND ENTROPIES OF SOLUTION OF H_2 AS A FUNCTION OF COMPOSITION IN THE TERNARY Zr–O–H SYSTEM

R^a	Phase region	Hydrogen composition, atom %	$\overline{\Delta S^0}$ of soln., cal./mole/°C.	$\overline{\Delta H^0}$ of soln., kcal./mole	Temperatures, °C.					
					600	700	750	800	850	900
0.068	α	31.4	−30.2	−39.6	..[b]	..[b]	10[b]	27[b]	60[b]	125[b]
	α	37.9	−31.9	−39.6	..	9	24	65	145	270
	$\alpha + \delta$	47.8	−43.2	−49.6	..	15	55	165	480	..
	$\delta + \epsilon$	57.2	....	....	15	140	290	472	..	..
	ϵ	60.4	....	....	100	450	660	..	..	..
0.121	α	30.4	−31.3	−39.6	..	..	18	48	100	212
	$\alpha + \delta$	42.1	−42.9	−49.6	..	13	45	150	455	..
	δ	48.6	....	....	6	53	150	342	605	..
	$\delta + \epsilon$	53.8	−27.1	−29.7	43	165	310	595	..	..
	ϵ	58.0	....	....	280	560	775	..	..	..
0.229	α	11.7	−23.2	−29.7	..	20	40	80	145	250
	α	16.6	−24.9	−29.7	..	46	95	200	325	510
	$\alpha + \epsilon$	39.8	−27.0	−29.7	35	135	300	515	..	..
	ϵ	53.0	....	....	285	485	648	..	..	..
0.328	α	5.8	−22.1	−29.7	..	12	24	49	85	155
	α	10.9	−24.5	−29.7	10	35	70	160	290	440
	$\alpha + \epsilon$	35.5	−27.0	−29.7	30	110	275	465	..	..
	ϵ	49.5	....	....	205	440	650	..	..	..
0.420	α	7.9	−24.9	−29.7	13	50	100	220	375	..
	$\alpha + \epsilon$	25.6	−26.4	−29.7	25	95	202	390	..	..
	ϵ	42.7	....	....	110	285	450	660	..	..

[a] R is the O/Zr atom ratio. [b] Pressures in mm.

change continuously in the one-phase region and also in the two-phase region, with a change in slope at the join of these regions, and it would finally change in slope at the boundary and remain invariant throughout the three-phase region.

An interesting consequence of the natural phase relations and the manner in which composition changes were effected in the present study is that for each material of a given R value, pressure–composition isotherms clearly indicate that the composition traverses were essentially along tie-lines in the two-phase regions. That this is not three-phase behavior can be seen by noting that pressures do actually vary in the regions indicated in Fig. 6 to be two-phase regions. A three-dimensional plot having the isothermal ternary diagram as a base and hydrogen pressure as the vertical ordinate would readily demonstrate this point. We have indicated the observed behavior in the ternary diagram by showing the two-phase regions shaded with lines presumed to closely approximate lines of constant hydrogen fugacity. Induction of the nature of the phase diagram was based on the above, and on the additional requirements that adjoining single-phase regions must be separated by a two-phase field and adjoining two-phase fields must be separated by a three-phase field. Room temperature X-ray diffraction patterns were taken on all of the fully hydrogenated specimens and in all cases the ϵ-phase[5] accounted for all diffraction lines. In particular, and somewhat to our surprise at first, none of the ZrO_2 diffraction pattern was found for any of these specimens. The diagram given is consistent with this observation.

A preparation of $R = 0.121$, of such a hydrogen composition as to place it just inside the δ-region on the zirconium-rich side, was examined by X-ray diffraction at room temperature. The relative intensities and positions of the lines of the pattern, except for one line, could be reasonably well correlated with patterns of α-zirconium, assuming appreciable distortion of the lattice. However, the one additional line of medium to strong intensity and low Bragg angle was unmistakably present. The broadness of the lines, like that generally found[7] in the patterns taken on materials in the binary zirconium–hydrogen system, precluded more detailed structural analysis. One may refer to the X-ray diffraction patterns by Sidhu and McGuire[11] for an idea of the magnitude and nature of the changes in the diffraction pattern as hydrogen is added to hafnium metal and the δ-phase makes its appearance.

It is essential that the nature of the phase relationships and temperature variation of phase field boundaries be carefully considered before significance is assigned to the partial molal quantities listed in Table II. As may be ascertained from plotting (not shown) the data of Table I, the boundaries of the two-phase fields generally speaking shift with temperature. Therefore, in these regions the thermodynamic quantities derived from the hydrogen pressure variation with temperature should be considered "apparent," and they do not necessarily apply to either of the two phases listed. They are useful and of interest however for comparison with the related values of the zirconium–hydrogen binary system.[5] The values for the single-phase α-region are unambiguous and apply directly.

The fact that the partial molal heat of solution of molecular hydrogen appears to be constant at $\overline{\Delta H^0} = -39.6$ kcal. per mole for a very large region in the α-phase in both the binary and ternary systems is considered evidence against significant interac-

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

tion between the oxygen and hydrogen atoms within the zirconium lattice in this concentration range. The increase of the partial molal heat of solution in the α-region of R values greater than 0.121 to $\overline{\Delta H^0} - 29.7$ kcal., which appears to remain constant thereafter, is not understood. The apparent value for the partial molal heat of solution of molecular hydrogen in the $(\alpha + \delta)$ two-phase region in this system is found to be the same as found in the zirconium–hydrogen binary system.

Consideration of the several specific regions of applicability of the listed $\overline{\Delta H^0} = -29.7$ kcal. per mole of molecular hydrogen and of the nature of the temperature variation of the associated phase field boundaries leads to the estimate that this value of the partial molal heat probably applies to the ϵ-phase along its zirconium-rich boundary for R values greater than about 0.121.

We have not discussed the presence of the β-phase region in this ternary study since from the known binary zirconium–oxygen system behavior[4] it is most probable that the region would have been displaced to temperatures higher than those used in this study.

We urge a reasonable caution in the use of the diagram we present and wish to note in particular the uncertainty in the actual apex positions of the three-phase fields. The extent of the uncertainty may be easily inferred on noting the amount and nature of the extrapolation of boundaries to these apex positions. The extent of solution of hydrogen in the θ-phase is, of course, quite uncertain. The extrapolation to the $(\delta + \epsilon)$ two-phase field boundaries leads to boundary compositions of about 61 and 62 atom % hydrogen for the binary zirconium–hydrogen system. We suppose that the value 62 atom % given for the hydrogen-rich boundary is probably quite accurate since the linear extrapolation nicely parallels the isothermal composition isobars, one of which is shown for the pressure 760 mm. by the dotted line in the ϵ-region of Fig. 6. On the other hand, a strictly linear extrapolation of the data for the zirconium-rich $(\delta + \epsilon)$ border would have led to a composition only negligibly lower than 62 atom % so that it may well imply an extremely narrow corresponding region in the binary zirconium–hydrogen system. If the boundary were taken as linear through the data points plotted, it would imply the relationship that the hydrogen saturation limit of the δ-phase decreases in a manner which shows oxygen initially to replace hydrogen on a three-and-one-half to one atom basis. The rather extensive linear portion of the hydrogen-rich α-phase saturation boundary similarly considered implies that oxygen will replace hydrogen on a three-to-one atom basis.

In the α-zirconium hexagonal close-packed structure, one would suppose that the oxygen atoms would fill the octahedral interstices—the largest holes available. Apparently they cannot do so completely or the solubility limit of oxygen in zirconium in the binary zirconium–oxygen system would correspond to 50 atom %. The actual limit of 29 atom % would correspond to the filling of only about two out of every five available octahedral interstices in α-zirconium at saturation with oxygen.

On the other hand, hydrogen may be either in tetrahedral interstices or in the octahedral interstices. If it is in the latter, the hydrogen binary saturation composition of 50 atom % in the zirconium–hydrogen system would indicate that all available octahedral interstices are filled. It appears then that each oxygen atom which enters the lattice denies more of the interstitial sites to hydrogen than it does to oxygen itself. This would seem to indicate a form of repulsion through general lattice strain and to rule out any special stabilization one might have anticipated to arise from proximate hydrogen. Effects due to the difference in electron affinities between oxygen and hydrogen thus seem to be absent.

The dotted line in Fig. 6 represents the contour of an isothermal composition isobar for a hydrogen pressure of 760 mm. and is therefore our value of the "saturation" composition in the sense of Hall, Martin and Rees.[6] It is seen that oxygen does replace hydrogen on approximately a one-to-one basis as supposed, but this seems to carry no implication beyond that readily explicable in terms of normal composition relationships between the ϵ- and θ-phases.

Acknowledgment.—The authors are pleased to acknowledge the stimulation of interest and constructive criticism by Dr. Daniel Cubicciotti of North American Aviation Company.

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