over, in the solvent extraction studies, the highest absorbancy indices are associated with the lowest hydrogen ion concentrations, and in the continuous variation series the same trend is noted.

Katzin[11] feels that thiocyanic acid should be stronger in coördination than the ion pair (Na^+-NCS^-) and hence sixfold coördination should be more likely in the system $Co(ClO_4)_2$ + NaNCS in the presence of perchloric acid. Thus one may be able to rationalize the six to one complexing (if such does indeed occur) in terms of the effect of the strong acid ($HClO_4$), but the fundamental question of the source of the 620 mμ absorption is left unanswered.

One possible explanation lies in a charge transfer process. The 620 mμ absorption may be the result of transfer of an electron along one of the thiocyanate ligands to the solvent. The intensity, but not the wave length, might depend on the number of thiocyanates present, as is observed. In the absence of tests of such an hypothesis, however, it is probably best to withhold judgment.

Acknowledgment.—The authors thank J. C. Sternberg for the many helpful suggestions he has given.

EAST LANSING, MICHIGAN

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[11] L. I. Katzin, private communication.

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Zirconium–Hydrogen System: Some Thermodynamic Properties from a Heat Content Study[1]

BY THOMAS B. DOUGLAS

RECEIVED FEBRUARY 26, 1958

The relative heat contents of zirconium and five zirconium hydrides (24–52 atomic % hydrogen) were precisely measured over the range 0–900°. Appreciable hysteresis was observed only near the eutectoid temperature. After developing a method generally applicable to heterogeneous systems, the heats of isothermal hydriding throughout most of the range of temperature and composition investigated were derived. Several of the boundaries of the phase diagram also were derived from the thermal data and are found to be in reasonably good agreement with the published results found by other methods. The energies and relative stabilities of the high temperature crystalline forms are discussed qualitatively after estimating their disorder entropies.

Investigations of several alloy-like hydride systems have been reported by many authors during the past few years. In the case of the zirconium–hydrogen system recent investigations of equilibrium hydrogen pressures,[2-4] diffusion of hydrogen,[5] high temperature X-ray diffraction[6] and neutron diffraction[7] have provided valuable if somewhat conflicting evidence concerning the crystal structures, energies and limits of composition of the existing phases. In this paper a number of energy relations of this system are derived from recently measured heat contents of a few compositions. It has been possible to correlate extensively the thermal results with some of the reported equilibrium values and to examine critically many discrepancies found. The evaluation of a thermodynamic property by several independent methods is particularly desirable in the case of *solid* systems, where equilibration is often slow and frequently not achieved.

As a multi-phase material changes temperature, physical or chemical changes often occur whose heats of reaction constitute a major part of the energy change. If the components are virtually immiscible at some temperature but become miscible or otherwise interact reversibly at another temperature, it is possible to measure the change in heat content of such a mixture over the given temperature range, then repeat the measurement on the components in a separated condition so that they have no opportunity to interact, and from the difference alone find the heat of the reaction occurring when the mixture changes temperature. The precise heat content data used in this paper determine the *differences* among the heats of a number of such reactions in the zirconium–hydrogen system, and assuming one of the values as determined by another method, all the other heats of reaction can be evaluated. Similarly, a number of equilibria, some already known at one temperature, were evaluated over a range of temperature by use of the thermal data.

Experimental

The total impurities and corrected hydrogen contents of the zirconium and the five samples of zirconium hydrides whose heat contents were measured are given in Table I.

Sample 1 was crystal-bar zirconium obtained from the U. S. Bureau of Mines, Albany, Ore. Samples 2 and 6 were supplied by the U. S. Air Force, Wright Air Development Center, where their hydrogen contents were determined (to an estimated accuracy of ±0.5% of the hydro-

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[1] (a) Presented before the Division of Physical and Inorganic Chemistry, 133rd National American Chemical Society Meeting, San Francisco, Calif., April, 1958. (b) The measurements of heat content were sponsored by the Wright Air Development Center, Air Research and Development Command, United States Air Force, under Delivery Order No. AF 33(616)56-21, Project No. 7360. (c) Complete experimental details and data have been given by T. B. Douglas and A. C. Victor, *J. Research Natl. Bur. Standards*, **61**, 13 (1958) (RP 2878).

[2] E. A. Gulbransen and K. F. Andrew, *J. Electrochem. Soc.*, **101**, 474 (1954); *J. Metals*, **7**, 136 (1955).

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

[4] C. E. Ells and A. D. McQuillan, *J. Inst. Metals*, **85**, (Part 3), 89 (1956).

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

[6] D. A. Vaughan and J. R. Bridge, *J. Metals*, **8**, 528 (1956).

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

TABLE I

SAMPLES

Sample no.	Total impurities, wt. %	Corr. hydrogen content— Atomic %	x in "ZrHx"
1	0.09	0.0	0.000
2	0.25	24.5	.324
3	2.6	35.7	.556
4	1.9	41.2	.701
5	1.9	50.0	.999
6	0.25	51.7	1.071

gen) by three independent methods. Their principal impurities were 0.1% Fe and 0.06% C. Samples 3, 4 and 5 were supplied by Sylvania Electric Products, Inc., Atomic Energy Division. Their hydrogen contents were determined by two combustion methods which agreed on the average to ±2% of the hydrogen. Their principal impurities, determined by quantitative spectrographic analysis, averaged 0.5% Hf, 0.6% Fe, 0.3% C and 0.4% Si.

Using a precision Bunsen ice calorimeter, a silver-core furnace and a drop method described previously,[8] the heat content relative to 0° was measured at approximately 12 temperatures up to 900°. The sealed empty container, constructed of the alloy 80 Ni–20 Cr, was measured separately. Each value in Table II was calculated from the mean of 2.8 duplicate measurements (on the average) on the sample plus container.[1c] The average deviation from the mean was ±0.005 kcal. per mole of sample (approximately 0.1%) except at 560 and 575°, where the deviations were sometimes much larger.

Additive corrections were applied to the compositions, masses and heat contents of the hydride samples on the assumption of removing the interstitial elements C, N and O and replacing the remaining impurities atom for atom by Zr. Above 800° there were appreciable losses of hydrogen, necessitating corrections to the heat content. These corrections, which were evaluated from the changes in sample mass and the drift in successive heat measurements, averaged 0.06 kcal. per mole of ZrH_x at 850° and 0.11 kcal. per mole at 900°.

Methods of Deriving Properties.—The phase diagram is shown in Fig. 1 as drawn by the author after consideration of all the evidence referred to in this paper, but the shapes of the two boundaries indicated by dashed straight lines are believed to be considerably uncertain. The dotted vertical lines and their points indicate the compositions and temperatures for which heat content values are reported.[1c] The evidence[2,3] for the existence within the "γ" field of a narrow two-phase field, designated "$\delta + \epsilon$" by some authors but not shown in Fig. 1, has been disregarded because the measurements of heat content do not involve relevant compositions.

The heat contents relative to 0° are plotted against temperature in Fig. 2. If the graph is viewed with the heat content axis at the bottom, the broken-line curves form a series of idealized cooling curves plotted in the usual way.

Heats of Hydriding.—In Fig. 2 the difference in ordinates of two points has physical significance only if the points lie on the same curve. It is desirable to adjust the relative vertical displacements of the curves so that, in addition, the difference in ordinates of any two points on different curves represents the change in heat content when through chemical reaction the indicated change in composition of the hydride occurs. First, however, the system whose heat content is considered must be modified so that the change in composition can occur without the addition or removal of any substance. This may be done in various ways, but in order that heats of hydriding may be derived, the system must contain hydrogen gas. It was convenient to adopt as the modified system 1 ZrH_x + [1 − (x/2)]H_2(g), where "ZrH_x" indicates the overall stoichiometric composition of the hydride if two or more solid phases are present.

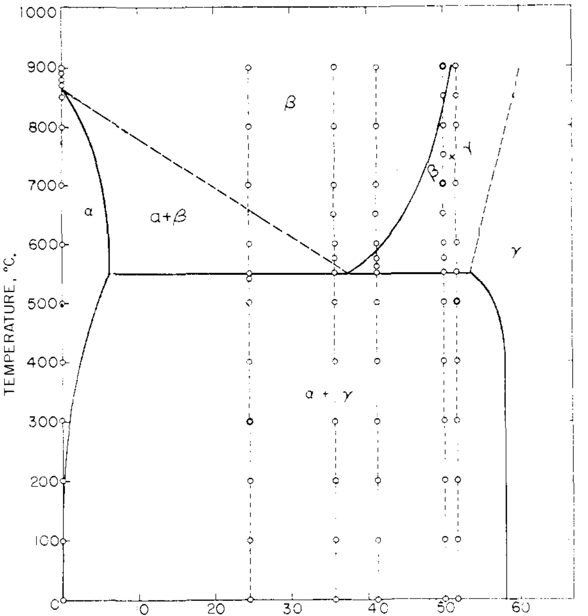

Fig. 1.—Phase diagram of the Zr–H system.

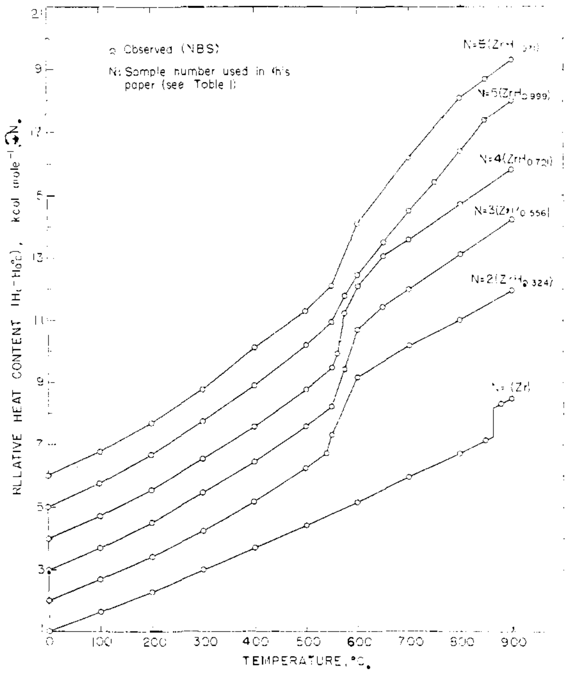

Fig. 2.—Heat content *vs.* temperature for several compositions of the Zr–H system.

If the modified system undergoes a hydriding reaction in which the hydride composition changes from $ZrH_{x'}$ to $ZrH_{x''}$, the net reaction is

$$1ZrH_{x'} + [(x'' - x')/2]H_2(g) = 1ZrH_{x''} \qquad (1)$$

If both hydrides lie within a one-phase field of the

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[8] G. T. Furukawa, T. B. Douglas, R. E. McCoskey and D. C. Ginnings, *J. Research Natl. Bur. Standards*, **57**, 67 (1956) (RP 2694).

phase diagram, the compositions of the two hydride phases are those of reaction 1. If, however, the reaction occurs isothermally and the two hydrides lie within a two-phase field whose boundary phases at that temperature have the compositions ZrH_a and ZrH_b, then regardless of the values of x' and x'' reaction 1 is actually the same reaction

$$[2/(b - a)]ZrH_a + 1H_2(g) = [2/(b - a)]ZrH_b \quad (2)$$

taken $(x'' - x')/2$ times. Furthermore, when the change in phase composition is discontinuous in this way, the determination of the heat of reaction 1 obviously determines the heat of reaction 2 without knowledge of the boundary compositions a and b.

The last step in adjusting the heat contents involves the determination of six constants, one of which is to be added to all the values of relative heat content for each hydride composition investigated. At 0° the six compositions may be assumed to lie within the two-phase $\alpha + \gamma$ field. Since the constants to be added are obviously equal to the final adjusted heat content values at 0°, they must be such that the difference between any two of them, when divided by the pertinent value of $(x'' - x')/2$, gives the same value for the heat of reaction 2 at this temperature. Thus the added constants (n_x) must vary linearly with x, and since one of them may be arbitrarily assigned, a single additional experimental datum is sufficient to determine the others. The evaluation of the constants n_x was completed by requiring that one heat of reaction derived by their use satisfy the variation with temperature of the reported equilibrium pressures of hydrogen. Greatest weight was given to the highest pressures, because these are ordinarily susceptible to the smallest percentage errors.

At a given temperature the "adjusted" heat content of the modified system, arrived at in this way and subsequently represented by H_x', is thus related to the molal heat content relative to 0° of the hydride ZrH_x and that of hydrogen gas, H_x and h, respectively, by the equation

$$H_x' = H_x + [1 - (x/2)]\,h + n_x \quad (3)$$

The partial molal heat of solution of hydrogen gas in the hydride (in phase field i) will be represented by ΔH_i, and is given by

$$\Delta H_i = 2(\partial H_x'/\partial x)_T \quad (4)$$

Limits of Phase Composition.—Two general methods employing the heat content data were used to determine several phase-diagram boundaries each separating a one- from a two-phase field. Because the heat content values are of high precision, it was convenient to apply these methods analytically.

The *first method* located, at the temperature in question, the intersection of the isotherms of adjusted heat content of the adjacent one- and two-phase fields. In terms of values for two given compositions $x = a$ and $x = b$ in these respective fields, the isotherms are, respectively

$$H_1' = H_a' + (\Delta H_1/2)(x - a) \quad (5)$$
$$H_2' = H_b' + (\Delta H_2/2)(x - b) \quad (6)$$

Setting $x = c$ at the phase-field boundary

$$= (b\Delta H_2 - a\Delta H_1 - 2H_b' + 2H_a')/(\Delta H_2 - \Delta H_1) \quad (7)$$

The *second method* located from the corresponding isotherms of hydrogen pressure

$$\ln p_1 = \Delta H_1/RT + \ln k_1 f_x \quad (8)$$
$$\ln p_2 = \Delta H_2/RT + \ln k_2 \quad (9)$$

their intersection at the boundary. The compositions along the boundary are thus given by

$$\ln f_c = \ln (k_2/k_1) + (\Delta H_2 - \Delta H_1)/RT \quad (10)$$

Equilibrium data at only one temperature were used to evaluate the ratio of constants k_2/k_1 and the function of x, f_x.

Results and Discussion

Adjusted Heat Content.—In evaluating the constants n_x the arbitrary reference point was chosen by setting $n_{1.071} = 0$. Replotting the pressures reported by Edwards, Levesque and Cubicciotti[3] from 700 to 900° for four equally spaced hydride compositions from $x = 0.65$ to 0.89 gave as the partial molal heat (ΔH) of solution of hydrogen gas −40.5 ±0.1 kcal.; this was assumed to be the mean value at 850° over the range $x = 0.556$ to 0.999, which lies entirely within the β phase field. The resulting added constants are represented by the equation

$$n_x = 22.614 - 21.115x \text{ kcal.} \quad (11)$$

The values of adjusted heat content for the six compositions investigated were calculated from equation 3 and are given in Table II. The parenthesized values were determined by interpolation in regions where there is strong reason to believe that the heat content varies almost linearly with temperature. When the nominal temperature of the hydride sample was approached not only by the usual procedure of heating, but also by cooling from a temperature 40 or 50° higher, the latter heats were always greater. In these cases the tabulated value corresponds to the average of the two means obtained by the two methods; a tolerance is stated equal to half the difference between the two means and may be assumed to express the uncertainty resulting from a lack of phase equilibrium. With the exception of those at 560 and 575°, the values investigated in this way are believed to be those having the greatest uncertainty from this source of error.

The values of Table II are plotted against the composition x in Fig. 3. The isotherms are shown by solid curves and dotted straight lines in the one- and two-phase fields, respectively. At any point the slope of the isotherm is equal to half the partial molal heat (ΔH) of solution of hydrogen gas in a zirconium hydride of the given over-all composition ("heat of hydriding"). The particular interval of abscissa that was used in evaluating the coefficients of equation 11 may naturally be appreciably in error, which, however, would lead to much smaller percentage errors in the slopes of the isotherms. At the $\alpha - \beta$ transformation temperature of zirconium (approximately 863°) the isotherm in the $\alpha + \beta$ field lies on the ordinate axis ($x = 0$), and its length necessarily equals the heat of transformation of 1 mole of the metal (0.89 kcal.[1c]).

The dashed curves which cut the isotherms in Fig. 3 at their points of discontinuity were derived as discussed below and correspond to the bound-

TABLE II

ADJUSTED HEAT CONTENT (H_x') OF THE SYSTEM 1 ZrH_x + $[1 - (x/2)]H_2(g)$

Temp., °C.	Adjusted heat content relative to that of $1ZrH_{1.071} + 0.4645H_2(g)$ at 0°, kcal.[a]					
	x = 0.000	x = 0.324	x = 0.556	x = 0.701	x = 0.999	x = 1.071
0	22.614	15.773	10.874	7.812	1.520	0
100	23.936	17.029	12.072	8.978	2.618	1.081
200	25.288	18.356	13.384	10.271	3.875	2.333
300	26.692	19.766	14.833	11.716	5.304	3.738
400	28.090	21.280	16.337	13.206	6.818	5.239
500	29.518	22.946[c]	17.987[g]	14.861	8.479[m]	6.919[q]
550	(30.241)	(23.820)[d]	18.886	15.785	9.400	7.919
560	(30.386)	....	....	16.287	....	....
575	(30.604)	....	20.212	17.659	10.325	....
600	30.966	26.460[e]	21.621[h]	18.644[j]	11.084[n]	10.066[r]
650	(31.710)	....	22.627[i]	19.821[k]	12.290	....
700	32.457	28.064[f]	23.435	20.602	13.473[p]	12.478
750	(33.205)[b]	(28.782)	(24.261)	(21.388)	14.586	....
800	33.966	29.503	25.089	22.177	15.759	14.706
850	34.756	(30.241)	(25.887)	(22.970)	16.916	15.489
880	36.136[b]	(30.686)	(26.367)	(23.447)	(17.396)	(15.951)
900	36.460[b]	30.982	26.687	23.765	17.717	16.258

[a] 1 kcal. = 4184.0 absolute joules. [b] Smoothed (using values for x = 0 only). [c] ±0.001. [d] Based on the value extrapolated from 540°. The value actually observed at 550° would give 24.295. [e] ±0.011. [f] ±0.002. [g] ±0.001. [h] ±0.152. [i] ±0.006. [j] ±0.069. [k] ±0.000. [m] ±0.009. [n] ±0.020. [p] ±0.012. [q] ±0.010. [r] ±0.017.

aries of the phase diagram (Fig. 1), the invariant eutectoid "point" here appearing as a triangle ("$\alpha + \beta + \gamma$"). The positions of these boundaries are not affected by any error in the one isotherm slope derived above from non-thermal data.

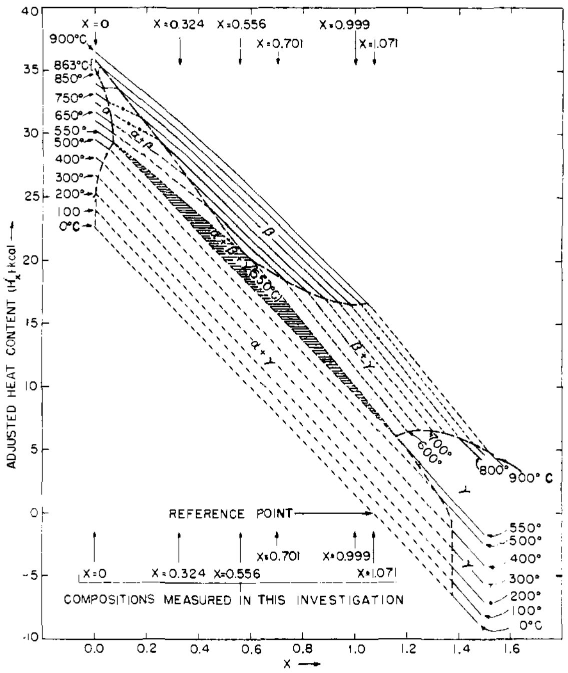

Fig. 3.—Adjusted heat content (H_x') *vs.* composition of the system 1 ZrH_x + $[1 - (x/2)]H_2(g)$.

The α, $\alpha + \gamma$ Phase Field Boundary.—The well-known additivity of extensive properties in two-phase fields is demonstrated by the observed values of relative heat content plotted against over-all sample composition in Fig. 4. According to Fig. 1 the five hydride samples lie inside the two-phase $\alpha + \gamma$ field up to 550°, but zirconium, which is essentially in this field at 0 and 100°, shows increasing deviations from the hydride isotherms of Fig. 4 as the temperature rises and the α field becomes wider. The equations of the $\alpha + \gamma$ isotherms, derived from the observed values by the method of least squares, are given in Table III.

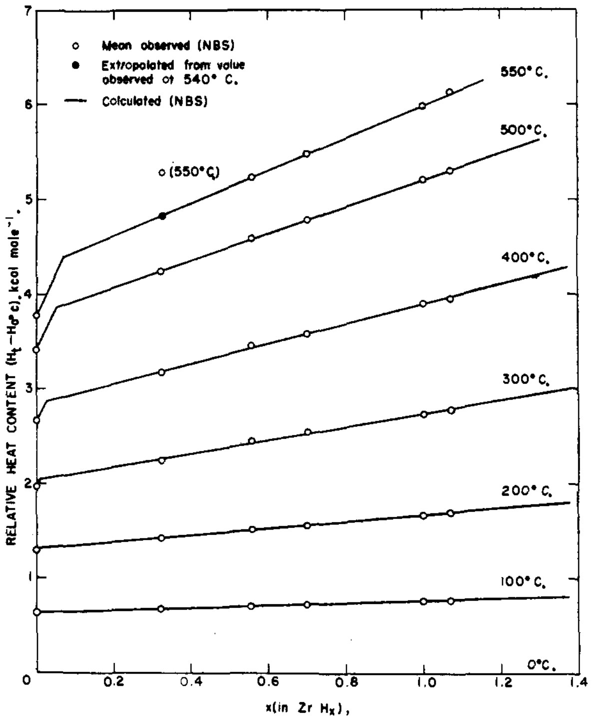

Fig. 4.—Heat content *vs.* composition of the Zr–H system, 0–550°.

The heat content of only one composition in the α field (zirconium metal) was measured. However, the α, $\alpha + \gamma$ boundary composition at 550° differs by only 3% as found by two different methods[2,5]; using the mean, equation 7 gives in the α field $\Delta \bar{H}_1 = -27.6$ kcal., which agrees exactly with one of the values reported by Gulbran-

TABLE III

SMOOTHED HEAT CONTENT IN THE $\alpha + \gamma$ PHASE FIELD

$H_x = A + Bx$ kcal. per mole of ZrH_x

Temp., °C.	A	B	Temp., °C.	A	B
0	0	0	400	2.8494	1.0397
100	0.6375	0.1140	500	3.7942	1.4100
200	1.3056	.3565	550	4.2770	1.7058
300	2.0418	.6949			

sen and Andrew[2] and may be assumed to be approximately independent of temperature and composition. With the assumption that in equation 8 $f_x = x^n$, where n is a constant to be determined, the boundary compositions found by the two methods using the heat contents are compared with the results of other methods in Table IV.

TABLE IV

THE α, $\alpha + \gamma$ Zr–H PHASE FIELD BOUNDARY BELOW THE EUTECTOID TEMPERATURE

Temp., °C.	Phase composition, atomic % hydrogen				
	Eq. 7	Eq. 10		From pressure[2]	From diffusion[5]
		$n = 1$	$n = 2$		
0	(0)	$5(10^{-8})$	$6(10^{-4})$	$5(10^{-5})^a$	0.002^a
100	0.10	$9(10^{-5})$	0.03	0.006^a	$.04^a$
200	.3	0.007	.2	$.09^a$	$.3^a$
300	.7	.1	.9	$.5^a$	1.1^a
400	2.1	.8	2.3	1.8	2.6
500	4.8	3.5	4.7	4.3	4.9
550	(6.2)	(6.2)	(6.2)	6.1	6.3^a

[a] Extrapolated.

Equation 10 clearly agrees much more closely with the other three methods when n is assigned a value of 2. This value conforms to the shapes of certain directly determined pressure isotherms of the Zr–H system[2,9] and agrees also with the decidedly exothermic nature of these hydrides because it indicates that their hydrogen behaves as atoms instead of dissolved diatomic molecules. Furthermore, the agreement in Table IV between equations 7 and 10 suggests that phase equilibrium was approximately reached in the heat content measurements, for equation 7 is much more sensitive to small deviations from phase equilibrium at the lower temperatures.

Above 550° the boundary of the α-field given in Fig. 1 is that reported by Ells and McQuillan.[4]

The β, $\beta + \gamma$ Phase Field Boundary.—As the temperature increases above 600° each of the four highest curves in Fig. 2 exhibits an abrupt decrease in slope. This may be interpreted as occurring approximately where the sample passes from a two-phase into the one-phase β-field, where the heat contents are applicable to evaluating equation 5. The direct pressure measurements[3,4] indicate that in the $\beta + \gamma$ field $\Delta H_2 = -50.8 \pm 0.1$ kcal. in the range 550 to 875°. In calculating the boundary compositions the values from equation 7 were averaged for the two compositions $b = 0.999$ (sample 5) and 1.071 (sample 6), and the numerical form of equation 10 was based on the smoothed pressure isotherms directly observed by Edwards, Levesque and Cubicciotti[3] at 850°. The results of the two methods are compared with those reported from other methods in Table V.

TABLE V

THE β, $\beta + \gamma$ PHASE FIELD BOUNDARY

Temp., °C.	Phase composition, atomic % hydrogen			
	Eq. 7	Eq. 10	From pressure[3,4]	From X-ray[6]
550	..	38	32	42
600	41.5	42	40	42.5
650	..	45	45	44
700	46	47	49	46
750	..	48.5	49.5	48
800	49.5	49.5	50	51
850	..	50.5	50.5	53
900	..	51	..	..

Considering that three of the four methods are based on widely different and entirely independent experimental techniques, the four sets of boundary compositions and their variation with temperature are in reasonable agreement. The values at 550° show considerable disagreement, but a weighted mean of 37.5 atomic % hydrogen was adopted as a provisional basis for further calculations.

At 550°, which is the eutectoid temperature, the heat content isotherms (equation 6) for the $\alpha + \gamma$ and $\beta + \gamma$ fields intersect at a composition of 53.6 atomic % H, which establishes a point on the γ, $\beta + \gamma$ boundary. According to equation 10 the hydrogen content along this boundary increases with temperature, for although the applicable function f_c is not well known, measurements of pressure[3] in the two adjacent phase fields indicate that $\Delta H_2 - \Delta H_1$ has a substantial negative magnitude. It is assumed that the reported[3] constant boundary composition 59 atomic % H is most reliable at the highest temperatures investigated (near 850°).

The γ, $\alpha + \gamma$ Phase Field Boundary.—According to the X-ray-diffraction investigation of Vaughan and Bridge[6] the hydrogen-poorest γ-phase contains approximately 58 atomic % H up to 400° but increasingly less at higher temperatures. The consistency of these results with the heat content data was examined by tentatively assuming this boundary composition over the whole interval 0 to 550°. After the heat contents calculated from Table III had been decreased by the heat contents of zirconium metal, their increments between successive temperatures were found to correspond to the Einstein characteristic temperatures for harmonic vibration given in the last column of Table VI.

TABLE VI

THE γ, $\alpha + \gamma$ PHASE-FIELD BOUNDARY

Temp., °C.	Cor. phase composition, at. % H	θ_E assuming 58 at. % H
0	(58.0)	1532
100	(58.0)	1412
200	(58.0)	1311
300	(58.0)	1275
400	(58.0)	856
500	56.6	<0
550	53.6	

The small drift of θ_E up to 400° may be attributed to the approximations made, but the sharp decrease above 400° strongly suggests that Table III has been erroneously applied to a composition which is inside the γ-field at these temperatures. The values of θ_E above 400° were corrected by an

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[9] A. Sieverts and E. Roell, *Z. anorg. allgem. Chem.*, **153**, 289 (1926).

extrapolation of those below this temperature, and the boundary composition at 550° previously found then gave in the γ field $\Delta H_1 = -45.1$ kcal. The corrected boundary compositions calculated from equation 7 are given in Table VI and are in close agreement with those reported from X-ray diffraction.[6]

The hydride $ZrH_{1.92}$, assumed to be a γ-phase, was calculated from the results of this paper to have a molal heat of combustion of 285.7 kcal. assuming that of zirconium metal[10] to be 261.5. The corresponding values from the direct calorimetry of Sieverts and his co-workers,[11] corrected to a hafnium-free basis, are 285.3 and 258.8 kcal., respectively.

The Eutectoid Phases.—The eutectoid temperature of the Zr–H system was reported as 547 ± 2° by Ells and McQuillan[4] and as 560 ±10° by Vaughan and Bridge.[6] The heat content[1c] of sample 2 showed an abrupt change between 540 and 550° and that of sample 4, between 550 and 560°. Adopting 550° for this invariant temperature, the results of this paper gave the following compositions and "adjusted" heat contents of the coexistent phases: α, 6.2 atomic % H, 29.332 kcal.; β, 37.5 atomic % H, 20.166 kcal.; γ, 53.6 atomic % H, 6.121 kcal. The corresponding heats (ΔH) of converting one phase into another at this temperature, in kcal. per mole of hydrogen gas absorbed, were found to be: α to γ, −42.7; α to β, −34.3; β to γ, −50.7. The "eutectoid" reaction, which occurs when most zirconium hydrides of fixed over-all composition pass the eutectoid temperature reversibly, is accordingly

$$0.509ZrH_{0.066}(\alpha) + 0.491ZrH_{1.154}(\gamma) = 1\ ZrH_{0.600}(\beta) \qquad \Delta H = +2.2 \text{ kcal.} \quad (12)$$

Assuming the hydrogen pressures directly measured for β-phases at 850°,[3] equation 8 gave 0.086 mm. as the invariant eutectoid pressure. Compared with the pressures in the $\alpha + \gamma$ field based on this value and given by equation 9 at 500–550°, the directly measured values of Gulbransen and Andrew[2] are 10–15% lower and those of Ells and McQuillan[4] are approximately 5% higher.

The β-Phases.—Under given conditions of temperature and pressure, the reported compositions of the β-zirconium hydrides in equilibrium with α-phases, hydrogen gas or γ-phases often differ from one investigator to another by larger amounts than can readily be attributed to systematic errors of measurement. The β, $\alpha + \beta$ phase field boundary is widely different as reported in two papers.[4,6] The values of the invariant eutectoid pressure resulting from three independent investigations[2–4] were found to show considerably better agreement than one would expect from the differences among the three respective compositions of the β-phases involved. And lastly, if the β, $\beta + \gamma$ boundary had been determined from equation 7 using the heat content data for only sample 5 or 6, the boundary composition c at each temperature would have been a little lower in the first than in the second case. However, at 850 and 900°, where both samples appear to lie in the one-phase β-field, their heat contents follow closely the β-field isotherms in Fig. 3 indicated by the other samples.

These facts can be explained simply by assuming that at a given temperature the β-phases in the different samples have energies which depend only on phase composition, but equilibrium hydrogen pressures which depend also somewhat on the nature of the sample and thus affect the compositions and proportions of the phases which can coexist. It seems likely that small amounts of impurities affect the hydrogen pressures of the β-phases more than those of the α- or γ-phases.

The phase diagram of the Zr–H system (Fig. 1) is similar to those of many common solid–liquid systems showing considerable solid-phase miscibility. One would expect the high temperature β-solid solutions to be analogous in certain respects to liquid solutions, and in fact equation 12 illustrates the considerable increase in energy and entropy when these solid solutions are formed from the low temperature phases. As hydrogen is added to such a β-solution, its conversion to a γ-solution ultimately occurs, with a marked decrease in energy and entropy. Like the β-phases, the γ-phases may for the sake of comparison be considered to have a body-centered tetragonal Zr lattice. The neutron-diffraction investigations of Rundle, Shull and Wollan[7] have shown that in the γ-zirconium hydrides (at least those approaching ZrH_2 in composition) there are two symmetrical sites for hydrogen atoms on each rectangular face of the Zr lattice, but none on the square faces. No similar directly determined information appears to be available for the β-hydrides, but a consideration of their entropies promises to be enlightening. Representing the number of hydrogen sites per Zr atom by Z and assuming that they have equal *a priori* probabilities, for m moles of ZrH_x the entropy S' attributable to disorder of the hydrogen is related to Z by the equation

$$S' = k \ln(ZmN)!/(xmN)!\,(ZmN - xmN)! \quad (13)$$

where k is Boltzmann's constant and N is Avogadro's number.

Effective values of Z in the β-zirconium hydrides of two reactions at 850° were derived from their standard-entropy changes (at 1 atm.) calculated from the interpolated pressure data of Edwards, Levesque and Cubicciotti.[3] The first reaction considered is

$$8.197ZrH_{0.650}(\beta) + 1H_2(g) = 8.197ZrH_{0.894}(\beta) \quad (14)$$

The standard thermodynamic equation $\Delta F^0 = \Delta H^0 - T\Delta S^0$ gave $\Delta S^0 = -31.8$ e.u. for reaction 14. Between 850 and 900° the molal heat capacities of the pertinent β-hydrides increase, on the average, by 3.26 cal./deg. per g.-atom of increase in hydrogen content; assuming this increase to be due mainly to the behavior of the hydrogen in the hydrides as a three-dimensional harmonic oscillator ($\theta_E = 3100$), the corresponding entropy of 3.0 e.u. per two g.-atoms was assumed to be the net gain in vibrational contribution to be subtracted from the value of ΔS^0 of reaction 14 in getting $\Delta S'$. After then adding the entropy of one mole of hydrogen gas, equation 13 led to a common value of $Z = 4.1$ for the two β-hydrides.

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[11] A. Sieverts, A. Gotta and S. Halberstadt, *Z. anorg. allgem. Chem.*, **187**, 155 (1930).

The second reaction considered is the hydriding at 850° of the H-richest β-hydride to form the H-poorest γ-hydride

$$4.587\text{ZrH}_{1.021}(\beta) + 1\text{H}_2(\text{g}) = 4.587\text{ZrH}_{1.457}(\gamma) \quad (15)$$

For this reaction $\Delta S° = -43.9$ e.u. Proceeding as for the first reaction except assuming that for the γ-phase $Z = 2$ and that the lattice contribution per g.-atom of hydrogen is the same for the two hydrides, it was found that for the β-phase of reaction 15 $Z = 2.9$.

The two values $Z = 4.1$ and 2.9 indicate effectively more hydrogen sites in the β than in the more ordered γ-lattice, for in the latter $Z = 2$. In fact, the β-Zr lattice is isotropic, and if there were two equivalent sites on *each* face, the value of Z would be 3. The estimated vibrational contribution to the entropy is somewhat uncertain, but the assumption of a higher value, *e.g.*, would decrease the first calculated value of Z and increase the second.

The progressive addition of hydrogen to a constant amount of one g.-atom of zirconium at some temperature above the α-phase field such as 900° is revealing. The heat evolved per mole of hydrogen added is smaller in the earlier than in the later stages, averaging only 34 kcal. from Zr to $\text{ZrH}_{0.3}$ but remaining approximately constant at 40 kcal. from $\text{ZrH}_{0.5}$ to ZrH. This difference is qualitatively explained if one assumes that the simultaneous expansion of the metal lattice, which itself is endothermic, occurs more rapidly at first, leading to a highly defect hydride lattice. In addition, the later stages of hydriding may liberate appreciable resonance energy reminiscent of the increasing heats of reaction when many chemical elements are oxidized in successive steps. The initial zirconium has a cohesive energy of approximately 120 kcal., but when the composition ZrH is reached, the cohesive energy of the solid has risen to approximately 190 kcal., and its structure must have become increasingly dependent on satisfying the requirements of the hydrogen for low energies. Further addition of hydrogen causes transition to a new Zr lattice. The new structure (γ) is evidently better adapted than the old (β) to efficient bonding with the now abundant hydrogen, and the large release of energy in the transition (51 kcal. per mole of H_2 absorbed) is great enough to offset the lower entropy of the new, more ordered structure and render it stable.

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Phase Separation in Metal–Ammonia Solutions[1]

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The separation at low temperatures of alkali metal–ammonia solutions of about 4% metal into two liquid phases has seemed surprising. However, if one regards the ammonia as a dielectric medium within which the alkali metal ions and valence electrons move, then the phase separation may be understood as a vapor–liquid condensation. This model is developed semi-quantitatively and is found to be consistent with the experimental properties of the solutions.

In 1907 Kraus[2] discovered that solutions of sodium in liquid ammonia separate into two liquid solution phases at low temperatures and for a range of composition near 4 mole % sodium. Later Kraus and Lucasse[3] determined the equilibrium compositions more accurately and measured in addition the electrical conductance of each phase. Some other metal–ammonia solution systems have also been reported to show phase separation. In particular calcium[4] and lithium[5] solutions do give phase separation, but cesium[6] solutions do not. The author is not aware of any published explanation of this surprising phenomenon.

Solutions of sodium, or similar metals, at high concentration in ammonia show the properties of liquid metals. Indeed many of these systems yield solid ammoniates, such as $\text{Ba(NH}_3)_6$, which behave as metals. These systems show specific conductance in the range 10^3 to 10^4 ohm^{-1} which is similar to the pure metals mercury and bismuth.

McConnell and Holm[7] extended and modified the model of Huster[8] and of Becker, Lindquist and Alder.[9] In the solutions of intermediate concentration the dominant species are assumed to be solvated metal atoms and diatomic molecules. The valence electron of the metal atom is assumed to be in a greatly expanded orbital which extends through several layers of the ammonia molecules which surround each positive metal ion. The analogy was made to the donor state in a semiconductor such as silicon. Similarly expanded diatomic molecules are formed as the concentration increases. This model is in qualitative

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[1] This research was performed under the auspices of the U. S. Atomic Energy Commission.

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