

The Thermodynamics of the System $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2 + \text{H}_2$ Using Heat Conduction Calorimetry

D. M. GRANT,¹ J. J. MURRAY,² AND M. L. POST

Division of Chemistry, The National Research Council of Canada, Ottawa, Ontario K1A 0R6, Canada

Received January 11, 1990; in revised form April 23, 1990

The system $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2 + \text{H}_2$ has been reported to exhibit one compound hydride phase $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2\text{H}_x$ with $x \geq 1.8$. The present *in situ* free energy/enthalpy measurements indicate a more complex situation involving two compound hydrides, one having the approximate composition $1.8 \leq x \leq 2.0$, and the other, $x \geq 2.3$. The steady state pressure-composition and calorimetric evidence for this is presented and discussed.

Introduction

Both ZrFe_2 and ZrCr_2 are Laves phases which form hydrides of the composition ZrM_2H_2 . The ZrCr_2 hydride is extremely stable compared with the ZrFe_2 hydride. The ternary system, $\text{Zr}(\text{Fe}_{1-y}\text{Cr}_y)_2$, which exists for $0 < y < 1$, exhibits intermediate H_2 equilibrium pressures and as a result use of a ternary unhydrided phase of selected composition allows very specific tailoring of the hydride properties. Some of these ternary phases exhibit the rapid kinetics, appropriate H_2 pressures at or near ambient temperature, and large hydrogen capacities, which are necessary for hydride applications such as hydrogen storage, heat pumping, etc. Because of this, pressure-composition-temperature (p - x - T , where x is the hydrogen content) studies of these com-

pounds have been made with a view to characterization for such applications. (1-3)

In this laboratory we have studied the detailed thermodynamics and crystallographic structures of selected compound hydride phases such as LaNi_5H_6 (4-6), CaNi_5H_6 (7-10), and Mg_2NiH_4 (11, 12) using *in situ* heat conduction calorimetry and *in situ* X-ray and neutron powder diffractometry. A calorimetric study of a $\text{Zr}(\text{Fe}_{1-y}\text{Cr}_y)_2 + \text{H}_2$ system ($y = 0.25$) is reported here as representative of AB_2 -type compound hydrides. Limited X-ray diffraction measurements for this system with $y = 0.25$, and some calorimetric studies for $y = 0.45$, were also made. These latter systems also have been reported to have at least two unusual characteristics: a very highly sloped "plateau" region (13) and an apparent solubility range of the compound hydride (β phase) which is exceptionally wide. $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2 + \text{H}_2$, the system studied most extensively in this work, has been reported to have an absorption plateau pressure at 298 K of approximately 1 \rightarrow 3 atm (1) and a single com-

¹ Present address: Oxford Research Unit, The Open University, Berkeley Road, Oxford OX1 5HR, United Kingdom.

² To whom correspondence should be addressed.

pound hydride which exists over approximately $2 < x < 2.85$ in $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2\text{H}_x$ for pressures of < 20 atm.

Experimental

Samples were prepared by arc melting 3 to 6 g of a mixture of the elements using a high purity evacuable arc melter and dry box handling procedures. Cr as pellets, and Fe and Zr as foils, were used as received from Alpha Chemicals and had a stated purity of 99.9% or better total, 99.95% or better metallic. The mixture was prepared with a 2% excess of Cr compared to the desired final stoichiometry, since Cr is substantially more volatile than the other elements at the estimated melting temperature. In addition, in order to minimize vaporization, the pellets of Cr were wrapped in strips of the Fe and then of the Zr foil for the first arcing. The evacuable arc melter was pumped to $< 10^{-8}$ atm prior to backfilling with 0.25 atm argon. After the initial melt, the boule was inverted and melted a second time. Selected samples were annealed at 1200 K for periods of 10–12 days in welded stainless steel containers backfilled with 0.25 atm argon. The argon used here and during arc-melting operations was purified to < 1 ppma O_2 by gettering over titanium at 900 K immediately before use. Samples were characterized for phases present using X-ray powder diffraction, for impurities by dc arc emission spectroscopy, and for stoichiometry via inductively coupled plasma atomic emission analysis.

Simultaneous pressure–composition (p – x) and enthalpy measurements were made by titrating H_2 gas in and out of the powdered hydride via an all welded, vacuum tight, stainless steel manifold held at 301.0 K. The samples were activated *in situ* by thorough evacuation followed by 3 hydride/dehydride cycles to ≈ 35 atm. The hydride was located in the measurement zone of a twin cell heat conduction calorimeter

held at 273.00 K. Details of the equipment and procedures have been described earlier, (4, 5, and 10). Pressures are measured to $\pm 0.1\%$ and the errors in the measured enthalpies range from ± 0.1 to ± 0.3 kJ $(\text{mol H}_2)^{-1}$ as $\delta p/\delta x$ varies from its minimum to its maximum. As in previous reports, enthalpies are given per mole of H_2 for convenience even though the hydrogen is combined atomically in such hydrides.

Results and Discussion

The atomic emission analysis confirmed that the stoichiometry of the phases obtained corresponded to the composition of the starting mixture, except for the Cr loss indicated by the weight loss described below. However, with an estimated error level of $\pm 3\%$, this technique is not sufficiently accurate to be definitive. The final sample weight after arc melting was always slightly less than the initial total weight of the elements, usually by an amount just smaller than the 2% excess of Cr used in the initial mixture. The dc emission spectroscopy showed the maximum total metallic impurities to be 0.2 at.%, with Sn as the major impurity at 0.1 at.%.

A total of four preparations of $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2$ were made, all of which gave powder X-ray diffraction patterns which were sharp (MoK α radiation, Debye–Scherrer mount, FWHM = 0.11, cf. FWHM = 0.10 for well-crystallized Si) which is characteristic of well-crystallized, homogeneous materials. For a representative sample, the diffraction pattern was indexed on an hexagonal cell, with lattice parameters $a = 5.0069(5)$ and $c = 8.1930(8)$ Å. The peak intensities (determined using the peak profile analysis procedures of Sparks (14)) showed an excellent fit to intensities calculated for the MgZn_2 Laves phase structure (15) which is in the space group $P6_3/mmc$ with Zr on the Mg sites and Fe and Cr randomly distributed on the Zn sites

TABLE I
 $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2$, $a = 5.0069(5) \text{ \AA}$, $c = 8.1930(8) \text{ \AA}$,
 $P6_3/mmc$

$2\theta_{\text{obsd}}$	$2\theta_{\text{calcd}}$	h	k	l	d_{obsd}	I_{obsd}	I_{calcd}
13.669	13.680	1	0	2	2.980	3	3
16.286	16.286	1	1	0	2.504	41	39
17.653	17.657	1	0	3	2.311	80	79
18.831	18.826	2	0	0	2.168	13	12
19.109	19.112	1	1	2	2.137	100	100
19.481	19.481	2	0	1	2.096	76	74
19.936	19.944	0	0	4	2.049	15	14
21.330	21.329	2	0	2	1.916	10	10
22.075	22.082	1	0	4	1.852	9	9
26.751	26.759	1	0	5	1.5331	4	5
26.965	26.953	2	1	2	1.5211	2	2
28.407	28.403	3	0	0	1.4454	8	8
29.234	29.233	2	1	3	1.4054	33	35
—	30.10	0	0	4	—	—	4
30.153	30.159	3	0	2	1.3653	27	26
31.484	31.484	2	0	5	1.3072	28	33
—	31.60	1	0	6	—	—	4
32.173	32.178	2	1	4	1.2799	6	7
32.917	32.913	2	2	0	1.2517	22	28
—	35.63	2	1	5	—	—	5
35.731	35.752	2	0	6	1.1560	12	11
36.594	36.588	1	0	7	1.1297	2	3
37.594	37.591	3	1	3	1.1007	13	16
38.184	38.187	4	0	0	1.0843	1	1
38.553	38.533	4	0	1	1.0743	7	8
38.793	38.783	2	2	4	1.0679	8	10
—	39.510	2	1	6	—	—	3
39.540	39.556	4	0	2	1.0481	3	—
—					—	—	1
39.993	39.991	3	1	4	1.0371	2	2
40.278	40.286	2	0	7	1.0301	1	1
41.685	41.693	1	0	8	.9968	3	4
42.919	42.911	3	1	5	.9694	2	2
43.744	43.722	2	1	7	.9520	2	3
—	43.94	1	1	8	—	—	4
43.983	44.018	4	1	0	.9471	5	—
—					—	—	4
44.608	44.591	3	2	3	.9345	7	9

Note. Guinier diffractometer, graphite monochromatized $\text{MoK}\alpha$ ($\lambda = 0.70930 \text{ \AA}$) radiation, 0.3-mm capillary, rotating, 24°C.

in the ratio 3/1. This data is given in Table I. Some samples had 2 or 3 very weak ($<3\%$ I/I°) diffraction lines which did not fit the MgZn_2 Laves phase structure. These were identified as the most intense lines of ZrN .

Taken together, these results indicate that the samples obtained after arc melting, one of which was used for the calorimetric measurements, were well-crystallized, homogeneous, single phase samples with the stoichiometry $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2$, and a metallic purity of 99.8 at.%. The traces of ZrN which were present should be inactive to hydrogen and as a result would only cause minor errors in the reported hydride compositions.

Figure 1 illustrates the p - x diagram for the $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2 + \text{H}_2$ reaction which was obtained during one of the simultaneous p - x and enthalpy measurement sequences with the sample at 273 K. The data for this hydride/dehydride sequence were obtained over a period of 21 days with steady state conditions obtained in both $\delta p/\delta t$ and $\delta q/\delta t$ after each gas aliquot, where q is the measured heat. The long term nature of these experiments necessitates a very precise attention to the attainment of a gas-tight gas titration enclosure, and to titration procedures under well-controlled temperatures, all of which ensure accurate maintenance

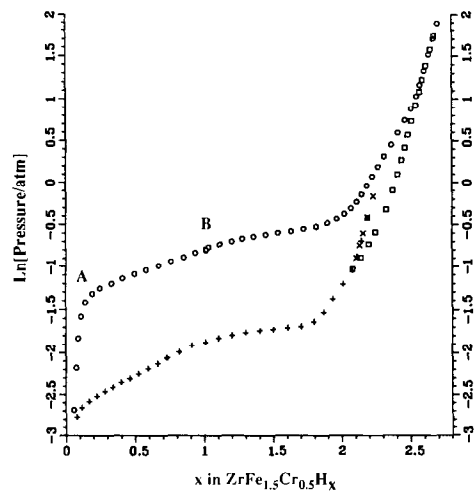


FIG. 1. Pressure-Composition plot for $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2\text{H}_x$ at 273 K. x is the final composition of each gas aliquot. \circ , absorption; \square , initial desorption; \times , reabsorption; $+$, continuation of desorption.

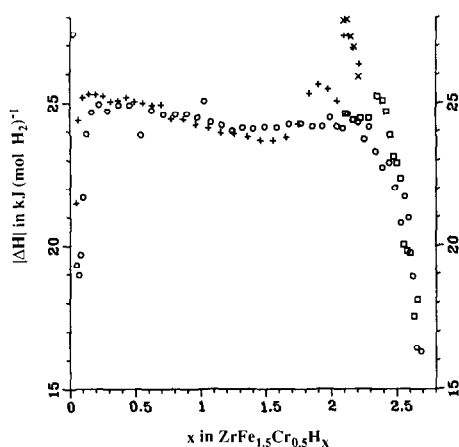


FIG. 2. $|\Delta H|$ vs x for $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2\text{H}_x$ at 273 K. x is the average composition during each gas aliquot. Corresponding p - x data given in Fig. 1. ○, absorption; □, initial desorption; ×, reabsorption; +, continuation of desorption.

and monitoring of the gas inventory and purity. A necessary, and in a practical sense, sufficient, indicator that such integrity has been achieved is that compositional closure is obtained at the conclusion of the measurement sequence. It is clear from Fig. 1 that such a closure was obtained in these measurements.

This steady state p - x diagram, and its accompanying ΔH vs x diagram, are the best thermodynamically interpretable data available, given that true equilibrium diagrams are not attainable for this type of gas-solid system, since they generally exhibit significant hysteresis. A detailed interpretation of most published p - x diagrams could be misleading, since, being obtained in much briefer, 1- to 3-day, experiments, they may contain anomalous features of kinetic rather than thermodynamic origins. Features apparent in Figs. 1 and 2, on the other hand, are true steady state features. Some of these features are particularly remarkable when compared to aspects of other compound hydride systems for which steady state p - x diagrams are also available.

The hysteresis in the region of lowest slope of p vs x ($0.15 < x < 2.0$, see Fig. 1), which is taken to be a two-phase coexistence region, is large,

$$\ln(p_{\text{abs}}/p_{\text{des}}) = 3.45,$$

where p_{abs} and p_{des} are the median absorption and desorption pressures, respectively. This compares to a value of 0.73 for LaNi_5H_x (5). As well, this "plateau" is markedly sloped, with

$$\ln(p_{a2}/p_{a1}) = 0.90 \text{ and } \ln(p_{d2}/p_{d1}) = 1.00,$$

where p_{a1} , p_{a2} and p_{d1} , p_{d2} are the absorption and desorption pressures at the lower (1) and upper (2) bounds of this region (see Fig. 1). For LaNi_5H_x these values are 0.02. Such characteristics were reported earlier by Ivey and Northwood (1).

A notable feature is the persistence of the pressure hysteresis well beyond the obvious marked change in slope in the p - x curve (at $x \approx 2.0$ in absorption), which is normally taken to be a boundary between a two-phase coexistence region and a single-phase region. In this region where $x > 2.0$ (in absorption), p - x reversibility only occurs for $x > 2.5$. Such a persistence of the pressure hysteresis has not been observed in the true steady state p - x diagrams available for other hydride systems such as $\text{LaNi}_5 + \text{H}_2$ (5, 16) and $\text{CaNi}_5 + \text{H}_2$ (7, 10). Most theories of the p - x hysteresis phenomenon (17, 18) are based upon behavior of a two-phase mixture and hysteresis within a single phase hydrogen solution is not predicted. This observation alone is suggestive that the composition range $2.0 < x < 2.5$ (in absorption) is also a two-phase coexistence region.

A second notable feature is the clear point of inflection (at $x \approx 1.0$) within the region of lowest slope in both absorption and desorption. Indeed, the notably high slope of the $\ln p$ vs x plot for this two phase region is largely a feature of the portion from $x \approx 0.15$ to $x \approx 1.0$. Above

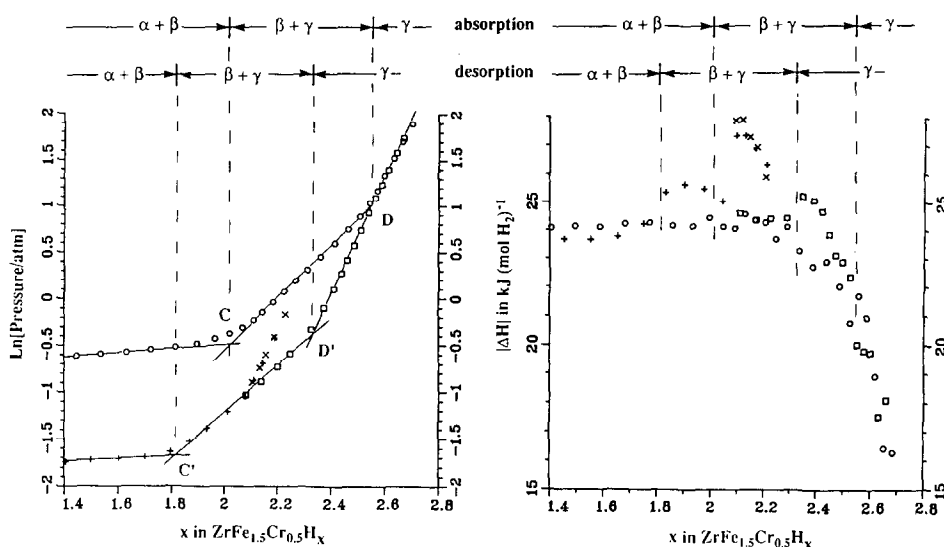


FIG. 3. Detail of p - x and $|\Delta H|$ plots for $x > 1.4$ in $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2\text{H}_x$, showing the inferred phase regions. \circ , absorption; \square , initial desorption; \times , reabsorption; $+$, continuation of desorption.

$x \approx 1.0$, the slope is similar to that typically seen for the hydriding of binary intermetallics. Finally of note is that within the higher slope portion, $0.15 < x < 1.0$, the slope of $\ln p$ vs x in desorption is substantially greater than in absorption.

Figure 2 illustrates the enthalpy data obtained simultaneously with the p - x results in Fig. 1. Figure 3 shows the details for the region of greatest interest, $x > 1.5$, in which the p - x features described above occur. A second complete absorption/desorption sequence was done for this material which actually preceded the scan reported in Figs. 1-3. The results for this preceding scan are completely consistent with the results reported here. Another preliminary scan using a composition $\text{Zr}(\text{Fe}_{0.55}\text{Cr}_{0.45})_2$ showed similar features.

The Region $x > DD'$

This is the region with $x > D$ in absorption and $x > D'$ in desorption. From the p - x portion of Fig. 3, in addition to the inflection points C and C' at $x = 2.05$ and $x = 1.8$,

which were taken by previous workers to be the lower boundaries of a single phase region, there is another pair of inflection points D and D', at $x = 2.57$ and $x = 2.30$, within this apparent solution region. For compositions greater than D and D', this system exhibits the fully reversible behavior in both p - x and $|\Delta H|$ - x characteristic of a simple solution process. As has been observed for many other compound hydrides the value of $|\Delta H|$, the relative partial molar enthalpy of solution decreases rapidly within this region with the increasing hydrogen content, reaching a value of $16 \text{ kJ} (\text{mol H}_2)^{-1}$ at the upper bound for these measurements, $x = 2.69$, $p = 6.62 \text{ atm}$. During the desorption in the first measurement series, a reabsorption/desorption sequence (RADS) was done beginning at $x \approx 2.46$, for a $\Delta x \approx 0.15$. Both the p - x and $|\Delta H|$ - x results showed complete reversibility. Based upon these results one can conclude unequivocally that the region above DD' is a simple hydrogen solution into a compound hydride designated here as the γ phase.

The Region $CC' < x < DD'$

Even though the p - x diagram exhibits a steep slope in this region, many characteristics typical of a two-phase coexistence region are present. They are

— $\ln p$ vs x , in both absorption and desorption, exhibits distinct slope changes at both boundary compositions.

—The region exhibits a substantial p - x hysteresis.

—A RADS over $\Delta x \approx 0.15$, starting from the desorption portion of the main scan in the region $D'C'$, shows clear interplateau behavior (19) in both the p - x and $|\Delta H|$ - x data.

The clearly present hysteresis, an attribute associated with two-phase coexistence (17, 18), and the corroborating observation of interplateau behavior (19) are convincing evidence that this is a two-phase coexistence region.

As shown by Bowerman *et al.* (19), during the initial portion of an interplateau sequence which starts from the desorption plateau, added hydrogen dissolves in both phases without any interphase conversion occurring. This simultaneous solution process, without phase conversion, generally continues until roughly 80% of the transition to the absorption plateau has occurred. During this stage the process is completely reversible. As shown in Fig. 3, the first reabsorption point gives a $|\Delta H|$ of 27.8 kJ (mol H_2)⁻¹, 3 kJ (mol H_2)⁻¹ higher than for the immediately preceding desorption point. Subsequent hydrogen additions (x 's) lead to rapidly diminishing $|\Delta H|$ values with x . The following desorption (+ 's) yielded complete reversibility in both p - x and $|\Delta H|$ - x with sharp discontinuities in both when the desorption "plateau" was reattained.

The two-phase coexistence shown by this data corresponds to a steady state condition, and, in desorption, is between forms of the γ phase and some other phase. Because of the rapidly dropping pressures of

this two-phase region "plateau," the γ phase will have a lower hydrogen content than at the phase boundary D' . Thus, the observed values of $|\Delta H|$ during the RADS are higher than any observed for the γ phase in the $x > DD'$ region, because of this reduced hydrogen content of the γ phase and the observed rapid decrease in $|\Delta H|$ with increasing x for the γ phase. These observed values of $|\Delta H|$ do not fall along an extrapolation of the values of $|\Delta H|$ observed for $x > DD'$ because during RADS there is a coexisting phase which is also dissolving or releasing hydrogen. The identification of this other phase is problematical.

The pronounced p - x slope changes at C and C' indicate a phase boundary at these compositions in absorption and desorption, respectively. The $|\Delta H|$ - x results in absorption are featureless at the composition D whereas the enthalpy results in desorption show small but clear peaks over several hydrogen aliquots in $|\Delta H|$ associated with both D' and C' . Such discontinuities are consistent with two-phase/single-phase boundaries at these points. The failure to observe these enthalpy discontinuities in absorption is probably due to smearing of the enthalpies associated with these boundaries caused by irreversible formation of the single phases during the briefly elevated pressure periods needed in the hydrogen titration. Such smearing has been observed before (5, 10, 16). Finally, if one assumes that this region is a two-phase conversion between phase γ and a phase β with a hydrogen solution along the CC' line with a $|\Delta H|$ of solution of ≈ 25.8 kJ (mol H_2)⁻¹, the p - x and $|\Delta H|$ - x effects observed in the RADS are predicted.

The evidence presented above is consistent with there being two compound hydrides, β and γ , in this system at 273 K with values of x of 1.8–2.05 and >2.33 , respectively. The small compositional difference between these phases could yield the high slope in the p - x data in their coexistence region. Confirmation of this interpretation

by *in situ* X-ray diffraction (or other appropriate technique such as neutron diffraction) is necessary.

Using the *in situ* apparatus and techniques which we have described earlier (9, 20), two series of hydrogen absorption/desorptions were attempted at room temperature for $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2$. In both cases the initial hydrogen addition to pressures which should have given a composition well within the γ phase gave X-ray diffraction patterns showing two coexisting phases with the same lattice type as the unhydrided phase. The major component had lattice parameters much greater than the unhydrided phase and the minor component ($\approx 10\%$) had parameters approximately equal to those of the unhydrided phase. This agrees with the previous results of Ivey and Northwood (1). However, in both attempts, the subsequent pump out did not lead to reversal of the reaction. Indeed, the reaction system appeared to be completely poisoned. This lack of reversibility makes these results inconclusive and uninterpretable in terms of confirming or denying the phase relations indicated by the calorimetric study, since the extent of hydrogen absorption corresponding to the diffraction results is unknown.

Since no such irreversibility was experienced in the all-welded, bellows-valved stainless steel apparatus used for the calorimetry, very thorough degassing procedures of the glass capillary portion of the X-ray apparatus were employed for the second *in situ* attempt. No improvement in the poisoning was observed. The sensitivity of this system to poisoning was also reported by Ivey and Northwood (1). Neutron diffraction probably could resolve this problem since *in situ* studies can be made using an all metal apparatus which can be readily degassed.

The Region $A < x < CC'$

In this region $|\Delta H|$ decreases smoothly and reversibly from about $25.2 \text{ kJ (mol H}_2\text{)}^{-1}$

at the lower composition boundary, $x \approx 0.2$, to about $23.8 \text{ kJ (mol H}_2\text{)}^{-1}$ at the upper boundary, $x \approx 1.9$. This region, ideally, should exhibit a reversible, constant enthalpy of conversion, $|\Delta H_c|$, since it is a two-phase conversion between the α phase and a compound hydride. However, in a "plateau" region exhibiting significant slope of $\ln(p)$ vs x , each hydrogen aliquot causes, in addition to conversion between the two phases, a change in the hydrogen content of the phases. As a result, instead of a constant $|\Delta H|$, one will observe a $|\Delta H|$ which varies across the "plateau," depending upon the relative proportions of the two solution processes which occurs and the values of $|\Delta H_s|$ of these processes. In this system the apparent α solution region ($x < 0.1$) is very narrow causing $\delta p/\delta x$ to be very large. Consequently, very little α solution will occur as the pressure rises during the two-phase conversion. Therefore the decrease in $|\Delta H_c|$ across the two-phase conversion would be largely due to increased solution of hydrogen in the compound hydride and is consistent with the partial enthalpy of solution, $|\Delta H_s|$, decreasing rapidly with increasing hydrogen content. Indeed the measurements for $x > \approx 1.8$ showed that the compound phase γ and the proposed phase β both exhibit substantial hydrogen solubility, i.e., a relatively low $(\delta p/\delta x)$. Furthermore the γ phase does exhibit a very rapidly decreasing $|\Delta H_s|$ with increasing x ; insufficient direct data is available to determine $\delta(|\Delta H_s|)/\delta x$ for the proposed β phase.

The present results show that, in addition to the large hysteresis and high slope of the p - x data for this region, reported by others, there are also clear changes in the p - x characteristics at B , $x = 1$ (Fig. 1). As described earlier, these results were obtained over 21 days and, therefore, correspond to steady state conditions for each gas aliquot. Since the slope of $\ln(p)$ vs x , in both absorption and desorption, is much higher for $x < 1$ than for $x > 1$ (see Fig. 2), it is clear that

the phenomenon causing the highly sloped plateau is not occurring uniformly across this region.

In contrast, the $|\Delta H_c|$ vs x data for this region shows excellent reversibility throughout without any measureable feature associated with the composition $x = 1.0$. This observation makes it unlikely that the change in slope of $\ln(p)$ vs x is caused by an event correlatable to the equilibrium state of this system, i.e., to the existence of a phase at $x = 1$. The substantial pressure change across this two-phase region and this clear change in $\delta p/\delta x$ at $x \approx 1$ both imply inhomogeneity. However, as described earlier, the samples of $\text{Zr}(\text{Fe}_{0.75}\text{Cr}_{0.25})_2$ exhibit X-ray diffraction patterns which index as a single phase and have diffraction line widths characteristic of a homogeneous well-crystallized material. Furthermore, even after hydriding, these materials show very little line broadening. Given that Fe and Cr have very similar X-ray scatter coefficients and similar atomic/ionic radii, it is possible that inhomogeneity in their occupancy of the Zn sites in the MgZn_2 structure would not be detectable by X-ray diffraction. Put more generally, attaining full homogeneity for many transition metal ternaries may be very difficult to achieve, even with annealing near 1200 K, and any resulting inhomogeneities may be difficult to detect. Alternatively, the sample may be fully homogeneous and, as discussed by Oates and Flanagan (21), such a sloped "plateau" is due to other causes associated with local equilibrium.

The α Solution Region, $x < A$

The desorption data indicate an upper limit for this region of $x = 0.08$. There is insufficient data available to characterize the enthalpies in the α solution region. However, both the absorption and desorption data show that the $|\Delta H_s|$ at the phase bound-

ary is much less than the $|\Delta H_c|$ for the A/CC' region. This is expected behavior and has been observed in other systems, e.g., LaNi_5H_x (5, 16) and CaNi_5H_x (7).

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