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Thermodynamic characterization of the Zr–Mn–H system Part 1. Reaction of H_2 with single-phase $ZrMn_{2+x}$ C-14 Laves phase alloys

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Abstract

The reaction of hydrogen with $ZrMn_{2+x}$ has been investigated using reaction calorimetry for $x = -0.2$, 0, 0.5 and 1.0. The enthalpies for hydride formation and decomposition are equal in magnitude over the two-solid-phase region; their magnitudes decrease with increasing x. Hysteresis is large for all these intermetallics, approximately 3.0 kJ (mol H)$^{-1}$, and independent of x.

1. Introduction

Many workers have investigated the reaction of H_2(g) with the hexagonal C-14 Laves phase $ZrMn_{2+x}$ intermetallic compounds [1–10]; the results can be summarized as follows.

(1) The C-14 structure is reported to be retained over the range of stoichiometries from $x = -0.2$ to 1.8 [1–3] and the unit cell volumes decrease with increasing x.

(2) Within the homogeneity range the plateau pressures increase with x.

(3) The plateau H_2 pressures are found to increase in the two-phase region with hydrogen content and within the homogeneity range the increase increases with x.

The increase in plateau H_2 pressures with hydrogen content in the two-phase region (which will henceforth be referred to as sloping plateaux) has been observed in all investigations of this system irrespective of whether or not the intermetallic compound (IMC) had been subjected to a homogenizing anneal prior to the measurement of the isotherms [1]. Thus the sloping appears to be an inherent property of these systems. In the hydride phase the C-14 metal sublattice is retained and therefore the $ZrMn_{2+x}$–H systems are miscibility gap ones with critical points, although critical points have not so far been estimated from the shapes of isotherms or from X-ray parameters at elevated temperatures.

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A brief account of aspects of this research has appeared [10] where it was shown that the sloping of the plateaux is caused by a decrease in $|\Delta H_{\mathrm{plat}}|$ with n, where $n = \mathrm{H:ZrMn}_{2+x}$, and not by a decrease in $|\Delta S_{\mathrm{plat}}|$ with n. In this research further consideration is given to the origin of sloping plateaux. An earlier explanation which was given [11] has been shown to be incorrect [12]. Other explanations will be considered.

Wallace and coworkers [3–5] have reported markedly different ΔH_{plat} values depending upon whether they were determined from calorimetry or from van't Hoff plots. However, Uchida *et al.* [8] reported a plateau enthalpy value determined from the van't Hoff plot for one of these IMCs, *i.e.* $x = 0.8$, which agreed reasonably well with the value for $x = 0.7$ determined calorimetrically by the Wallace group [5] and they therefore concluded that the latter's van't Hoff-derived thermodynamic parameters must be erroneous. Recently, however, Zhang and Wallace [6] re-investigated this system and found that their newly determined calorimetric enthalpies did not show large discrepancies from van't Hoff values; they did not comment on the discrepancies which were reported earlier [4, 5]. The more recent calorimetrically measured enthalpies for $\mathrm{ZrMn_2}$ indicated that $|\Delta H_{\mathrm{f,\,plat}}|$ and $|\Delta H_{\mathrm{d,\,plat}}|$ differed, *e.g.* 21.6 and 22.7 kJ (mol H)$^{-1}$ respectively; they note that this is not unexpected, since these systems exhibit hysteresis. We do not concur with these conclusions because it has been shown from basic thermodynamic considerations that there should not be a *significant* difference between the magnitudes of the two calorimetric values [13].

In this research we report calorimetric enthalpies for hydride formation and decomposition with the dual purpose of comparing the magnitudes of these enthalpies and of learning how they depend upon x. The ZrMn_{2+x}–H system has been shown to have a large isothermal pressure hysteresis [1, 3, 10], $\frac{1}{2}RT\ln(p_{\mathrm{f}}/p_{\mathrm{d}}) \approx 3.0$ kJ (mol H)$^{-1}$, and if the calorimetric enthalpies were to be significantly affected by hysteresis, this is an excellent system for the detection of such an effect. We also report thermodynamic parameters for this system at infinite dilution of hydrogen for activated samples which have been subsequently annealed at about 1100 K in order to remove defects introduced by activation. Such an annealing treatment allowed thermodynamic parameters for conditions of infinite dilution of hydrogen to be determined without a significant contribution due to hydrogen–defect interaction for $\mathrm{LaNi_5}$–H [14, 15]. In an accompanying paper we present some thermodynamic results for alloys which lie in the zirconium-rich and manganese-rich two-phase fields adjacent to the single-phase homogeneity region of the ZrMn_{2+x}–H Laves phase compound.

2. Experimental details

The ZrMn_{2+x} IMCs were prepared by arc melting the elements in an argon atmosphere. In each preparation a 5% excess of manganese above the intended composition was employed in order to allow for manganese loss during melting. The alloy buttons were annealed for 3 days at 1035 K *in vacuo*. After hydriding and dehydriding (activation), the samples were fine powders which were pyrophoric when exposed to the atmosphere.

The IMCs with $x=0$ and 1.0 were analyzed for their manganese contents using atomic absorption spectroscopy and very close agreement with the expected stoichiometry was obtained. X-ray powder diffraction revealed that the samples were hexagonal and the lattice parameters for $x=-0.2$ to 0.5 agreed with the values given in the literature but the value for $x=1.0$ differed somewhat.

The twin-cell differential heat flow calorimeter which was employed for the calorimetric studies has been described elsewhere [16]. All the calorimetric data were determined with samples which had been activated, *i.e.* samples which had been hydrided at about 10 atm (50 °C) and then dehydrided for 12 h at 250 °C.

The p–n–T data were determined using a conventional Sieverts-type apparatus capable of obtaining a vacuum of 10^{-3} Pa.

3. Results and discussion

3.1. *Unit cell volume as a function of x*

Figure 1 shows the unit cell volume as a function of x at 298 K from the present and other research. It can be seen that the volume changes continuously with x in the homogeneity region but outside this region the volumes become constant. The alloys in the present work have all been annealed. The data of the present investigation, which appear to be more consistent than those from the other studies, suggest that the homogeneity range is $-0.3<x<1.2$ with an error of about 0.1. We will compare these

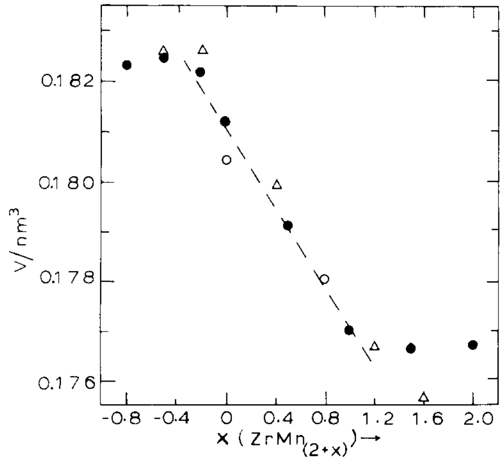

Fig. 1. Plot of unit cell volumes of $ZrMn_{2+x}$ against x: ●, present data; △, ref. 1; ○, ref. 4.

limits of homogeneity with values determined thermodynamically in an accompanying paper [17].

3.2. *Hydrogen solubility in the dilute phase*

Activated samples were annealed at about 1100 K. This annealing treatment largely, but not completely, eliminated non-zero intercepts with the abscissa in plots of $p^{1/2}$ *vs.* n. After subtracting small, but different, values of H:$ZrMn_{2+x}$ for each IMC from the experimental data of each value, the remaining dilute phase solubility data are seen to intersect the origin (Fig. 2). The slopes of the $p^{1/2}$ *vs.* n plots will not be affected by this procedure and their temperature dependences have been employed to determine values of ΔH°_H and ΔS°_H. Results are shown in Table 1, where it can be seen that the enthalpy at infinite dilution becomes less exothermic with

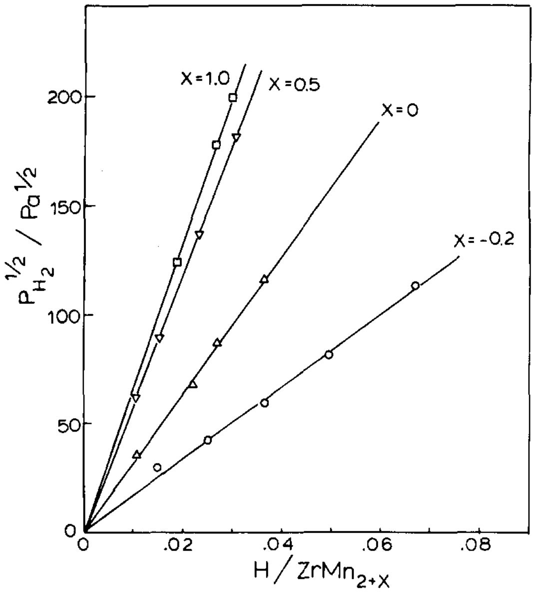

Fig. 2. Dilute solubility data for $ZrMn_{2+x}$; a small, constant value of n has been subtracted from each set of data to allow for some trapping at very small hydrogen contents.

TABLE 1

Values of ΔH°_H (kJ (mol H)$^{-1}$) and ΔS°_H (J K^{-1} (mol H)$^{-1}$)

x	$-\Delta H^\circ_H$	$-\Delta S^\circ_H$ ($\beta = 1$)	$-\Delta S^\circ_H$ ($\beta = 12$)
−0.2	8.0	37.7	58.0
0.0	5.9	35.1	55.7
0.5	4.0	36.3	57.0
1.0	4.2	36.6	57.3

x, paralleling the behavior of the calorimetrically determined plateau enthalpies (see below, Table 2).

The entropy values shown in Table 1 for infinite dilution in the third column have been calculated from

$$\Delta S_{\mathrm{H}}^{\circ} = \frac{\Delta H_{\mathrm{H}}^{\circ}}{T} - R \ln\left(\frac{p^{1/2}}{r}\right) \tag{1}$$

which tacitly assumes that there is one interstice per formula unit of ZrMn_{2+x}. Since only the tetrahedral interstices with two Zr and two Mn atom nearest neighbors are believed to be occupied [18] and because there are 12 of these per formula unit, $R \ln(12)$ should be subtracted from the values in column 3 giving the entropies shown in column 4. The entropies in column 4 are all about -57 J K^{-1} (mol H)$^{-1}$, which is a reasonable value, *e.g.* it is closer to the values for other M–H systems than those calculated assuming $\beta = 1$.

3.3. *Isotherms for the $x = 0$ IMC from 273 to 473 K*

Figure 3 shows absorption isotherms for the IMC with $x = 0$ from 273 to 473 K. It can be seen that the miscibility gap decreases with increasing temperature. This supports the fact that this (and presumably the other ZrMn_{2+x}–H systems) is a miscibility gap system in agreement with the X-ray diffraction results, which show that the Laves phase C-14 sublattice remains after hydride formation. The critical temperature for the stoichiometric compound ZrMn_2 can be estimated to be in the range between 550 and 600 K.

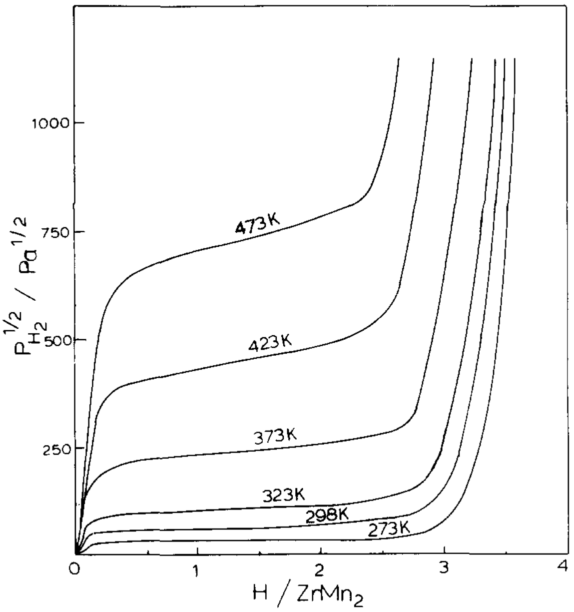

Fig. 3. Absorption isotherms for the stoichiometric compound $\mathrm{ZrMn}_{2.0}$, $x = 0$.

It can be seen that the sloping of the isotherm at 473 K is greater than that at 273 K. It should be noted, however, that the parameter reflecting the degree of sloping which is of more fundamental thermodynamic significance is $\partial\mu_H/\partial r$ and not $\partial p/\partial r$. When the slopes at the different temperatures are compared on the basis of values of $\partial\mu_H/\partial r$, they are quite comparable.

3.4. Isotherms and calorimetric results at 323 K

Absorption isotherms and calorimetric enthalpies for the IMCs are shown in Figs. 4–7 at 323 K, where it can be seen that both the degree of sloping and the magnitude of the plateau pressures tend to increase with x. Some of these results were shown on a single plot with an expanded ordinate scale in an earlier publication [10]; this earlier plot showed more clearly the increase in the degree of sloping with x. It is caused by a decrease in $|\Delta H_{plat}|$ with n and not by an increase in $|\Delta S_{plat}|$. This conclusion may not be as apparent in Figs. 4–7 because of the scale. These figures, however, feature calorimetric results for decomposition and for hysteresis scans not shown in the earlier condensed plot [10].

Figures 5–7 show that when hydrogen is desorbed at the end of the absorption plateau after 100% conversion to the β phase, the pressure decreases slowly to the decomposition plateau and the magnitudes of the enthalpies are greater than the plateau values, until the pressure corresponds to values on the decomposition plateau and then the magnitudes of the enthalpies are the same as for hydride formation. The change from the absorption to the desorption plateau requires that a relatively large amount of hydrogen be removed, indicating that $(\partial\mu_H/\partial r)_T$ is relatively small compared with, for example, its value in the α phase. It is of interest that in the $ZrMn_3$–H system shown in Fig. 7, hydride decomposition commences at a greater plateau pressure than that at which the hydride phase first forms.

The plateau reaction for hydride formation can be written as

$$\tfrac{1}{2}H_2(g) + \frac{1}{b-a}\,ZrMn_{2+x}H_a \longrightarrow \frac{1}{b-a}\,ZrMn_{2+x}H_b \qquad (2)$$

where the reverse reaction corresponds to hydride decomposition. The phase boundary compositions a and b both increase as the total hydrogen concentration in the two-phase region increases according to the results of Ivey and Northwood [19], who found that the X-ray parameters of the coexisting phase of a related Laves phase compound increased with fraction of conversion to the hydride phase. It would also be expected on thermodynamic grounds that if μ_H of a system increases at constant temperature and hydrostatic pressure, then its hydrogen content must increase.

For the IMCs with $x = -0.2$ and 0 there is an initial region (Figs. 4 and 5) where the H_2 pressures are negligibly small for the pressure gauges used here, *i.e.* below 1 Pa, and where the ΔH_H values are about -40 kJ (mol H)$^{-1}$. This does not correspond to a zirconium phase because the enthalpy of reaction with zirconium is much greater than -40 kJ (mol H)$^{-1}$ and because hydrogen cannot be removed from ZrH_2 by the pretreatment

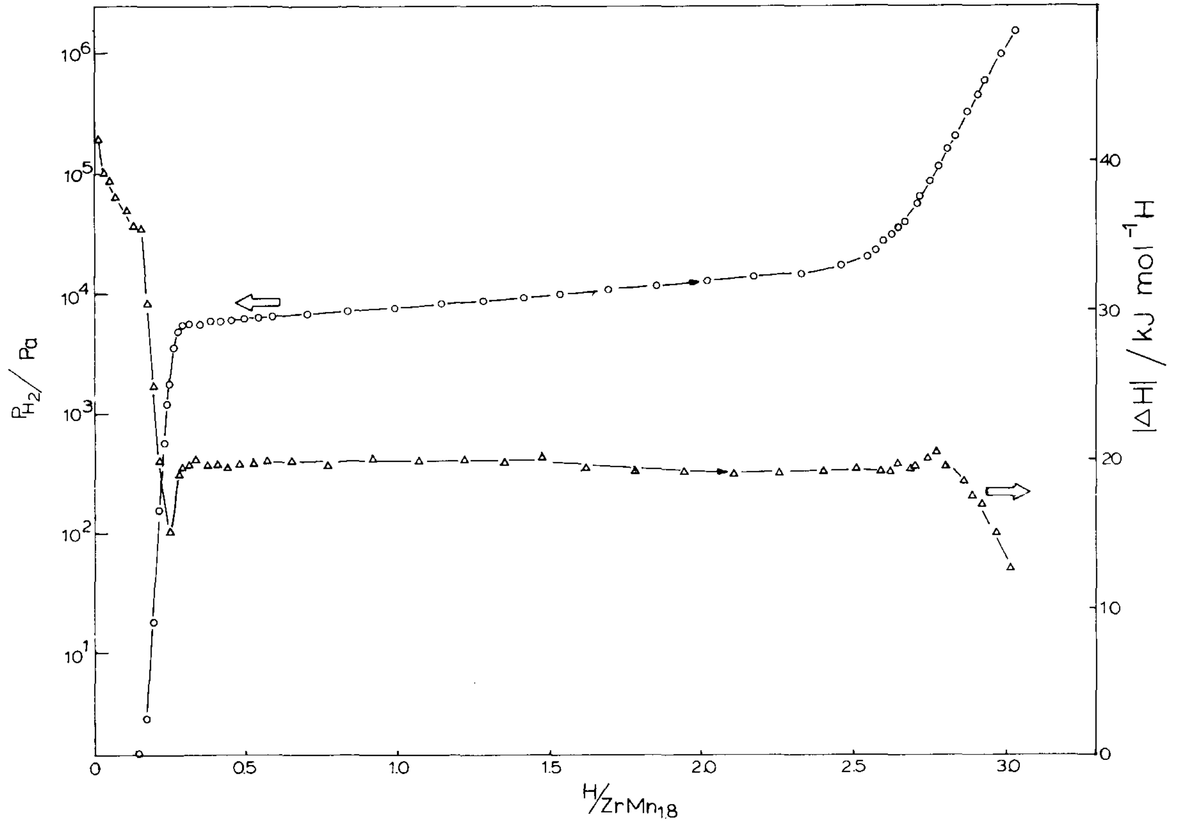

Fig. 4. Calorimetric data and equilibrium pressures for the absorption of hydrogen by the $ZrMn_{1.8}$ alloy at 323 K.

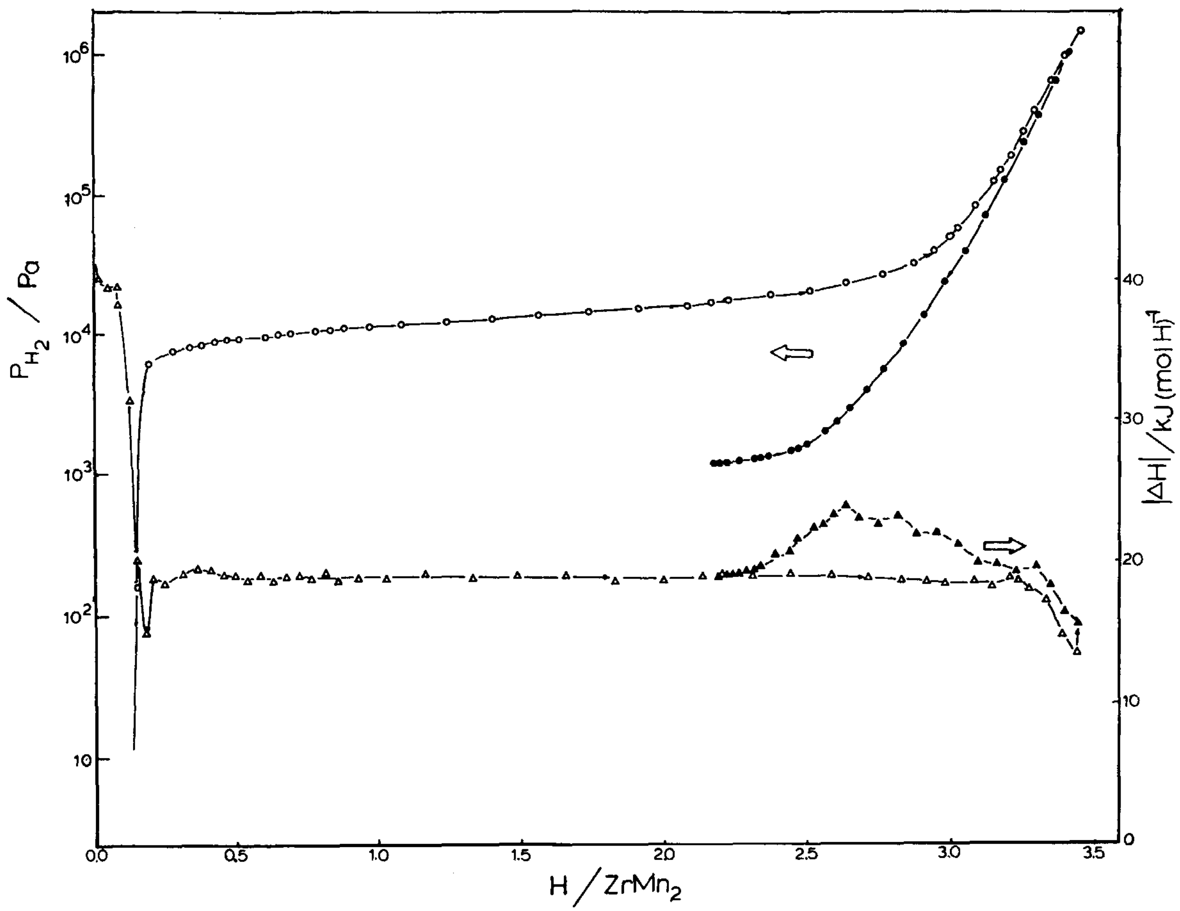

Fig. 5. Calorimetric data and equilibrium pressures for the absorption and desorption of hydrogen for the $ZrMn_{2.0}$ alloy at 323 K. Open symbols are for absorption and filled ones for desorption.

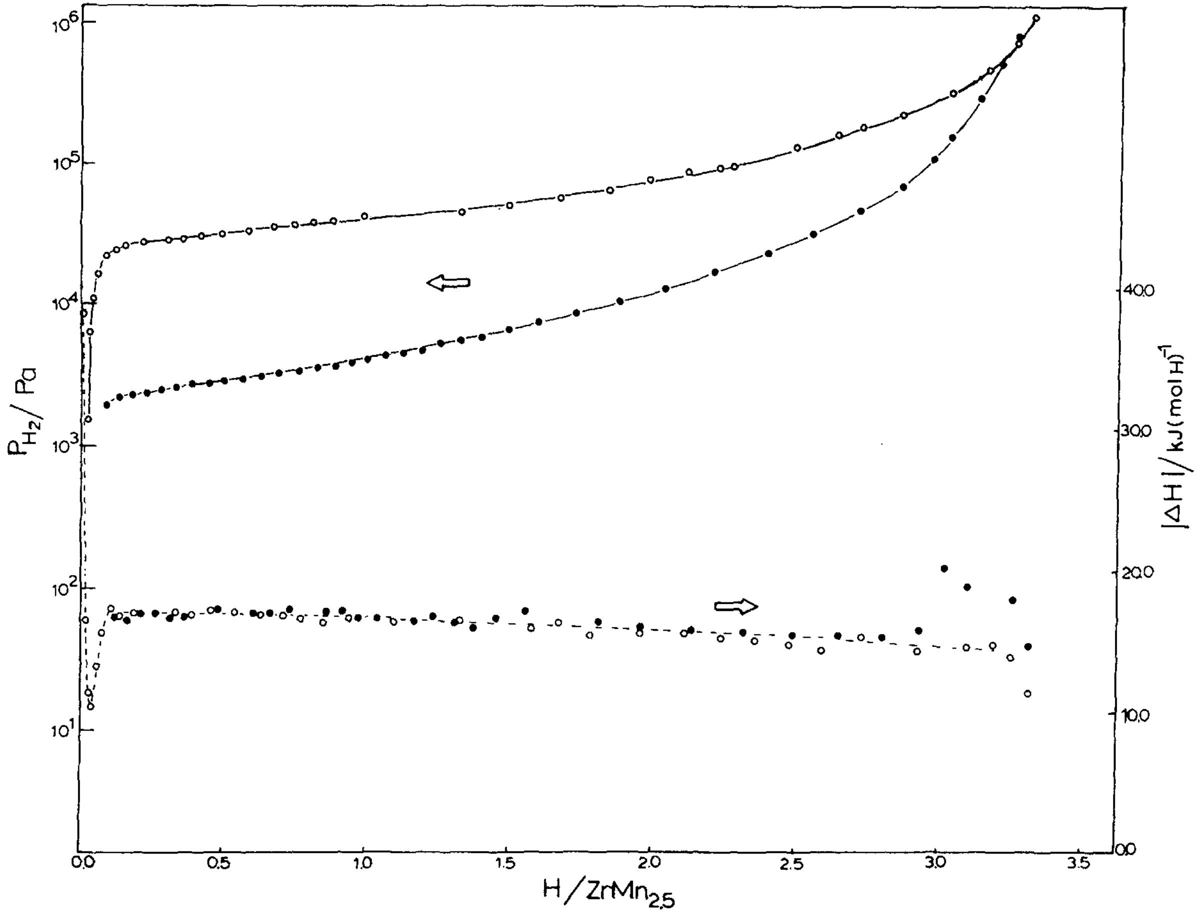

Fig. 6. Calorimetric data and equilibrium pressures for the absorption and desorption of hydrogen for the $ZrMn_{2.5}$ alloy at 323 K. Open symbols are for absorption and filled ones for desorption.

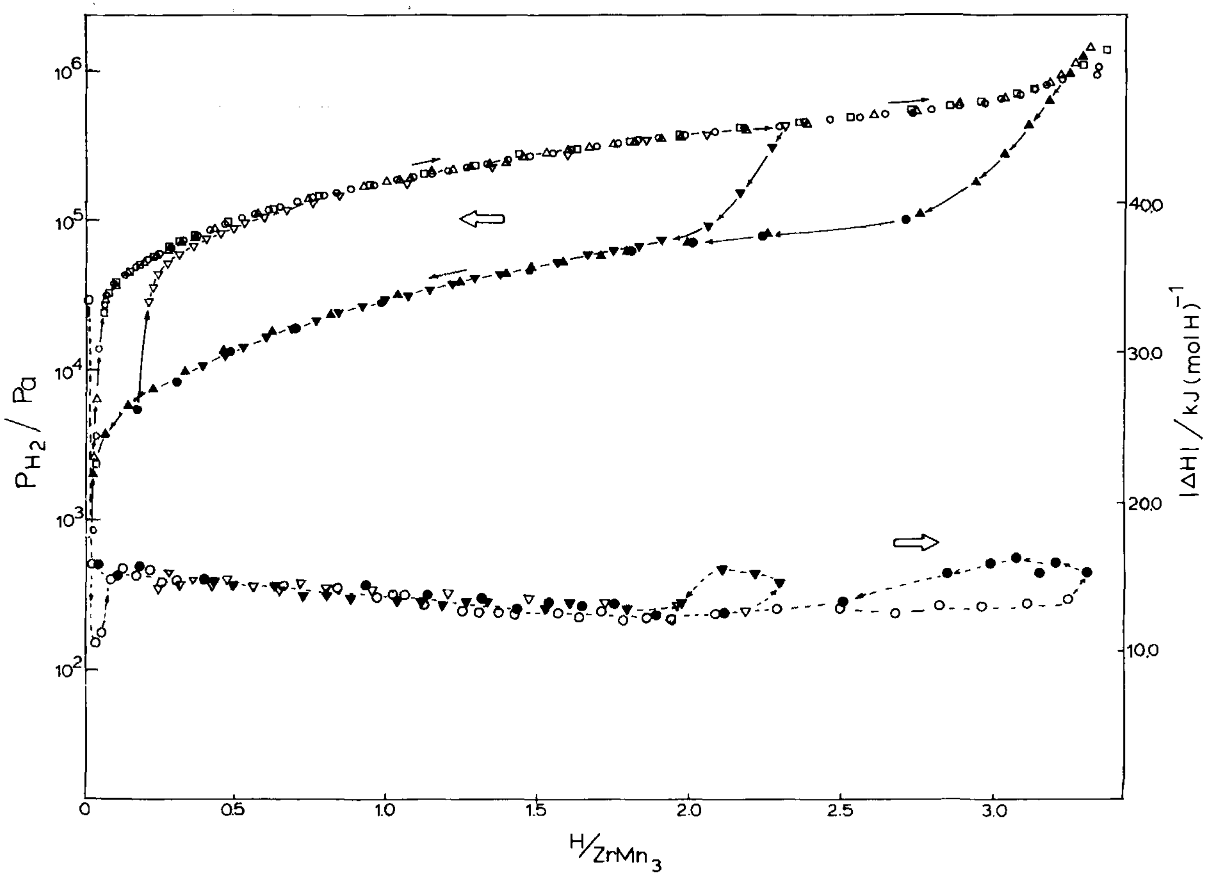

Fig. 7. Calorimetric data and equilibrium pressures for the absorption and desorption of hydrogen for the $ZrMn_{3.0}$ alloy at 323 K. Open symbols are for absorption and filled ones for desorption. Several desorption and absorption scans are shown.

employed on these samples, *i.e.* evacuation at 523 K. It is also not caused by defects introduced from activation because it is present to the same extent in both the activated and unactivated samples. Presumably it corresponds to some trapping sites initially present in the IMC, which would not be so likely to occur for the IMCs with $x > 0$, *e.g.* interstices surrounded by 3Zr and 1Mn rather than the usual occupied ones with 2Zr and 2Mn atoms as nearest neighbors.

Several hysteresis scans were undertaken before the end of the plateau region was reached (Fig. 7) and they also exhibited larger enthalpies than the plateau value, as would be expected because they reflect the coexisting single phases. Because of the relatively small value of $(\partial \mu_H/\partial r)_T$ for the β phase as compared to the value of $(\partial/\mu_H/\partial r)_T$ in the α phase, even when the fractions of the two phases are comparable, the measured enthalpies will reflect mainly those for the hydride phase during a hysteresis scan because most hydrogen must enter or leave this phase in order to maintain the equality $\mu_H(\alpha) = \mu_H(\beta)$. Similar results were found for the scan behavior of $LaNi_5$ [20].

In Fig. 5 it can be seen that when hydrogen is removed in the single-phase hydride region ($n \approx 3.4$), $|\Delta H_H|$ increases and passes through a maximum. The value of $|\Delta H_H|$ should then fall discontinuously to $|\Delta H_{plat}|$ when the hydride phase commences to decompose to the dilute phase; however, it does not, but instead falls continuously. This behavior may be caused for a reason analogous to the explanation of why a discontinuous change in enthalpies does not occur when the hydride phase first appears in the dilute phase region [21], *i.e.* the hydride phase starts to decompose at strained regions which have been introduced within the sample as a result of hydriding. In any case it is clear that there is a maximum in the value of $|\Delta H_H|$ in the $b-a$ interval and it would be observed if it were not masked by the two-phase region. For $ZrMn_3$ (Fig. 7) we were unable to fully convert the sample to the hydride phase because the pressure needed at 323 K exceeded the limits of the apparatus. Two hysteresis scans were carried out for this IMC (Fig. 7); it can be seen from one desorption scan and the original desorption data that the values of $|\Delta H_H|$ are greater than for the plateau value. This indicates for the scan that hydrogen is removed mainly from the hydride phase where the magnitude of its enthalpy is greater than that for the plateau value.

3.5. *Entropies evaluated from the calorimetric results and plateau pressures*

Relative partial molar entropies in single phases and relative entropies for the plateau regions have been calculated from the calorimetrically measured enthalpies and their accompanying hydrogen pressures, *i.e.*

$$\Delta S_H = \frac{\Delta H_H}{T} - \tfrac{1}{2}R \ln p_{H_2} = S_H - \tfrac{1}{2}S^{\circ}_{H_2} \qquad (3)$$

$$\Delta S_{\text{plat}} = \frac{\Delta H_{\text{plat}}}{T} - \tfrac{1}{2}R \ln p_{\text{plat}} = \frac{\Delta S_{\text{m}}(b) - \Delta S_{\text{m}}(a)}{(b-a)} - \tfrac{1}{2}S^{\circ}_{\text{H}_2} \tag{4}$$

where the standard designation refers to 1 bar of H_2(g) pressure. The principal motive for determining these is to show that the entropies in the plateau region are not a function of the overall hydrogen content, as shown by Fig. 8. Although it does not make any difference with regard to the demonstration of these trends of the entropy with n, the magnitudes of entropies in the plateau regions should not be obtained using eqn. (4) because of hysteresis, but instead only p–n–T data should be used [13]. If p–n–T data are unavailable, however, as in the present case, the avarage of the values of the formation and decomposition entropies are probably close to the value which would be expected in the absence of hysteresis. The average values are listed in Table 2 for those alloys where both formation and decomposition were measured and averaged. It can be seen that these do not exhibit any trends with x. It can be concluded that the entropies are affected neither by the sloping of the plateaux nor by the value of x and are very similar to values found in other systems for hydride formation and decomposition, *e.g.* Pd–H [22].

3.6. *Relation of plateau enthalpies to those at infinite dilution*

In Table 2 the differences between the plateau enthalpy values and those at infinite dilution are shown; it is seen that the differences are nearly constant at about -11 kJ (mol H)$^{-1}$. This difference contains the H–H attractive interaction which leads to the hydride phase formation from the dilute phase and it is of interest that this value is not unlike that for other miscibility gap metal–hydrogen systems, *e.g.* pure palladium–hydrogen (-9 kJ (mol H)$^{-1}$ [22]). The results in Table 2 confirm that hydride formation in the $ZrMn_{2+x}$–H system is analogous to that which occurs in pure metal hydrides, *i.e.* long-range H–H elastic interactions give rise to hydrogen condensation.

3.7. *Hysteresis*

An important point, which can be appreciated from Figs. 6 and 7, is that to within experimental error the magnitudes of the calorimetric enthalpies are equal for hydride formation and decomposition. It has been shown from thermodynamic arguments that there should be no *direct* effect of hysteresis on these enthalpies [13, 23]. This has been verified most recently for Nb–H, which has a very large hysteresis in the second plateau region [24]. The new result here is that even when both enthalpies change with n, they change by the same amount.

There is an *indirect* effect of hysteresis caused by the different phase boundaries which obtain for hydride formation and decomposition, *i.e.* the forward and reverse reactions are not exact opposites. The effect is superimposed on that caused by changes in n on ΔH_{plat} and the former is quite small by comparison. The result of Zhang and Wallace [6] which shows a

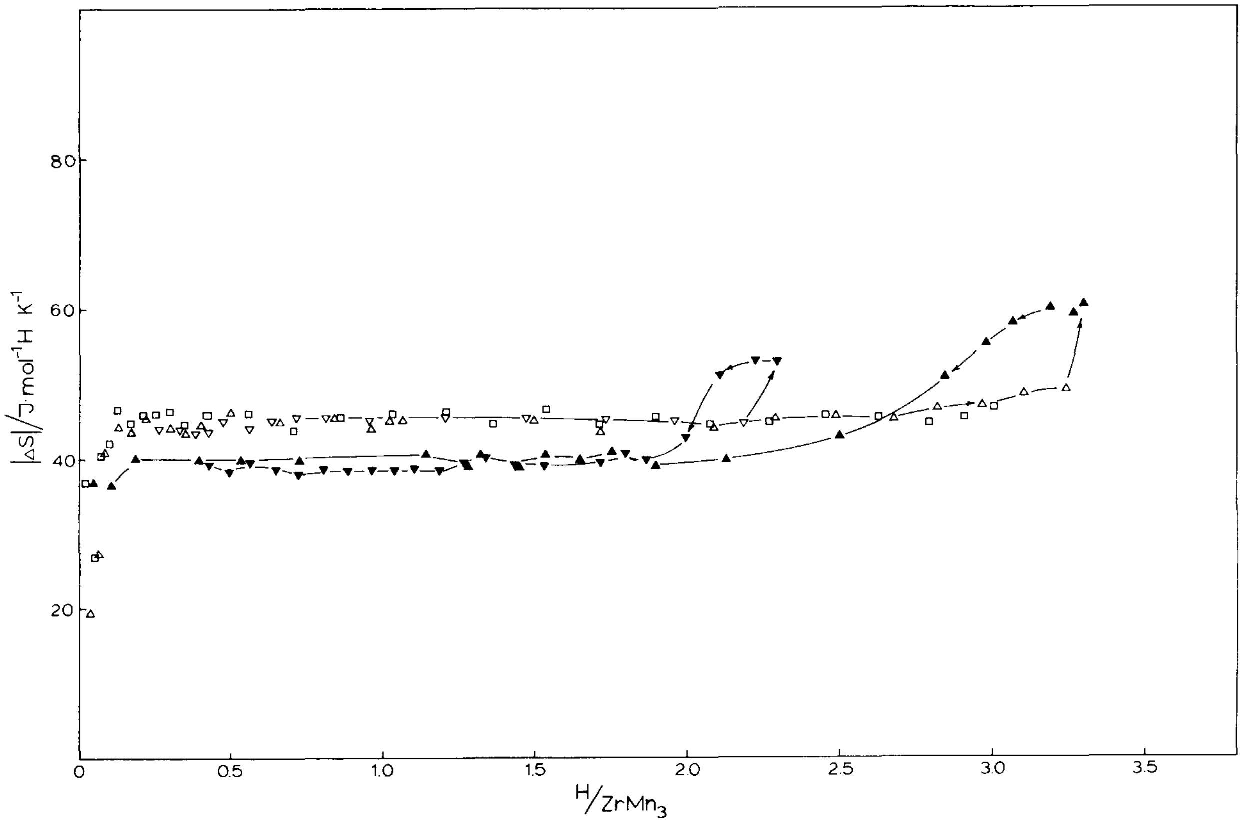

Fig. 8. Entropy changes during absorption (open symbols) and desorption (filled symbols) for $ZrMn_{0.3}$ at 323 K. Several scans are shown.

TABLE 2

Differences between $\Delta H^{\circ}_{\text{plat}}$ and $\Delta H^{\circ}_{\text{H}}$ for different values of x, and values of $|\Delta S_{\text{plat}}|$ (the enthalpies are in kJ (mol H)$^{-1}$ and the entropies in J K^{-1} (mol H)$^{-1}$; plateau values are evaluated at H:ZrMn$_{2+x}$ = 1.5)

x	$-\Delta H^{\circ}_{\text{plat}}$	$-\Delta H^{\circ}_{\text{H}}$	$-(\Delta H^{\circ}_{\text{plat}}-\Delta H^{\circ}_{\text{H}})$	$\|\Delta S_{\text{plat}}\|$
0.2	19.4	8.0	11.4	–
0	18.7	5.9	12.6	47.0
0.5	16.0	4.0	12.0	45.0
1.0	14.6	4.2	10.2	46.0

difference in these values comparable to the values for hysteresis, $\frac{1}{2}RT\ln(p_f/p_d)$, seems, therefore, questionable.

The extent of hysteresis, $\frac{1}{2}RT\ln(p_f/p_d)$, represents the work done on the system which is dissipated as heat during a hysteresis cycle expressed per mole of hydrogen. Because of the sloping plateaux, it is important that hysteresis be evaluated at the same dilute-to-hydride phase ratio and this may not be the case for the same overall hydrogen content because of differences in the phase boundary compositions caused by hysteresis, which, although small, may be a factor. Values for hysteresis at a fixed value of n are about 3 kJ (mol H)$^{-1}$. Hysteresis does not appear to change much with x except that the $x=0$ stoichiometry alloy appears to have a larger hysteresis than the others.

3.8. *Sloping plateaux*

Figure 9 shows pressure changes for hysteresis scans for the $x=1.5$ intermetallic compound. The plateau for this sample slopes very markedly and it can be seen that the sloping is maintained following a scan, *i.e.* if an absorption scan is carried out from the decomposition plateau, the system finishes at approximately the value of p_f found for the initial sloping formation plateau at that hydrogen content. When hydrogen is removed from this system, it then returns to the sloping decomposition plateau. The sloping therefore has a "memory" which is not eliminated by reversing the reaction. This demonstrates that the sloping is not caused by strain introduced by the progressive enclosure of the dilute phase by the hydride phase during hydride formation and vice versa during hydride decomposition. This may also indicate that the hydride phase forms at nuclei throughout the sample rather than from the surface inwards as might be expected. It appears as though a definite hydrogen chemical potential is associated with a certain fraction of conversion to the hydride phase.

As noted earlier, Ivey and Northwood [19] showed that the hydrogen content of the hydride phase for Laves phase alloys (Zr(Fe$_x$Cr$_{1-x}$)$_2$–H) increases with increasing fraction of conversion of the dilute to the hydride phase. This was established from small shifts to lower angles of the X-ray lattice parameters of the hydride phase as the fraction of conversion to the

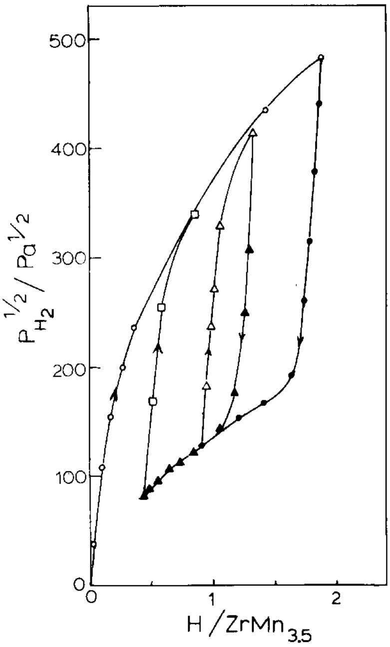

Fig. 9. Hysteresis scans for $ZrMn_{3.5}$. After each scan the sample is seen to return to the sloping plateaux.

hydride phase increases across the plateau and any successful explanation of sloping plateaux must explain this.

For a miscibility gap system such as $ZrMn_{2+x}$–H it would be expected that $|\Delta H_{\text{plat}}|$ should increase if the two-phase boundary compositions increase [11]. $|\Delta H_{\text{plat}}|$ is the average of $|\Delta H_{\text{H}}|$ over the interval $b-a$, *i.e.*

$$|\Delta H_{\text{plat}}| = \frac{1}{b-a}\int_a^b |\Delta H_{\text{H}}| \, \mathrm{d}n \tag{5}$$

Because of the fact that $|\Delta H_{\text{H}}|$ in the β phase hydride adjacent to the $(\alpha+\beta)$–β phase boundary is greater than the plateau value, an increase in hydrogen concentration of the hydride phase boundary will result in an increase in the average value, *i.e.* $|\Delta H_{\text{plat}}|$; the dilute phase boundary does not change as much owing to its greater value of $(\partial\mu_{\text{H}}/\partial r)_T$. Enthalpies measured during hysteresis scans or decomposition from the hydride phase (Figs. 5–7) also show that $|\Delta H_{\text{H}}|$ in the hydride phase is greater than the plateau values. The results of decreasing values of $|\Delta H_{\text{plat}}|$ with n conflict with these considerations; an explanation for the sloping must explain this.

It is useful to speculate about the microscopic thermodynamics of sloping plateaux in systems such as $ZrMn_{2+x}$. Explanations based on the presence of coherency at the interface do not appear to be satisfactory for sloping plateaux. Below we offer an explanation of how a spread in certain of the thermodynamic parameters can lead to sloping plateaux.

In a disordered, but macroscopically, homogeneous alloy there are different types of interstitial sites which will be selectively occupied by hydrogen since the energies for hydrogen solution will differ. It has been shown by Griessen and Driessen [25], however, that the presence of different site energies, by themselves, will not lead to sloping plateaux if the H–H interaction is a global, mean field one, *i.e.* if the interaction depends only on the total hydrogen content. Let us discuss how this limitation can be removed.

The different types of interstitial sites can be regarded as subsystems of the total system of interstitial sites. The chemical potential of hydrogen for a given subsystem i can be written as

$$\Delta\mu_{\mathrm{H},i}=\Delta\mu^{\circ}_{\mathrm{H},i}+RT\,ln\left(\frac{\theta_i}{1-\theta_i}\right)+\mu^{\mathrm{E}}_{\mathrm{H},i}(\theta_i) \tag{6}$$

where θ_i is the fraction of occupied sites in subsystem i, $\theta=\sum_{i=1} f_i\theta_i$, with f_i the fraction of sites of type i, and $\mu^{\mathrm{E}}_{\mathrm{H},i}(\theta_i)$ is the local excess chemical potential of hydrogen in sites of subsystem i.

If there are differences in the site energies, then it would seem that there should also be concomitant differences in the mean field intensities felt at the different types of sites. Thus we can write $\mu^{\mathrm{E}}_{\mathrm{H},i}=W_i\theta_i$, where W_i is a local mean field interaction energy. In the absence of knowledge of the fractions of the different types of sites, we have assumed a simple gaussian distribution. This leads to a similar gaussian distribution in the site energies and local interaction energies.

Sloping plateaux can result when there is a spread in both $\mu^{\circ}_{\mathrm{H},i}$ and $\mu^{\mathrm{E}}_{\mathrm{H},i}$ or only in the latter.

Values of the mean values and standard deviations were used as fitting parameters in comparison with the experimental results. In the evaluation of the θ_i the sites were considered fully occupied at $n=3.5$. Using this simple mean field model, the following values were obtained from fitting the model to the experimental results: $\langle\Delta\mu^{\circ}_{\mathrm{H}}\rangle/RT=4.22-710/T$ with $\sigma=0.025$ and $\langle W\rangle/R=1750$ with $\sigma=0.025$. In this fitting of these data the value of $\langle\Delta H^{\circ}_{\mathrm{H}}\rangle$ was taken from the results at infinite dilution (Table 1), but $\langle\Delta S^{\circ}_{\mathrm{H}}\rangle$ and the value of $\langle W\rangle/R$ were chosen for $\Delta\mu^{\circ}_{\mathrm{H}}=\Delta H^{\circ}_{\mathrm{H}}-T\Delta S^{\circ}_{\mathrm{H}}$. It would not be expected that the value of $\langle\Delta S^{\circ}_{\mathrm{H}}\rangle$ found at infinite dilution would be applicable to the hydride region.

A comparison of the calculated results with this simple model calculation is shown in Fig. 10. It can be seen that the agreement with the results shown in Fig. 3 is quite reasonable, *i.e.* the phase boundary compositions, the plateau pressures and the degree of sloping are all reproduced quite well.

In order for the fit to have significance, there must be a reasonable physical explanation of the spread $\Delta\mu^{\circ}_{\mathrm{H}}$ and W/R. It seems difficult to believe that these IMCs would be inhomogeneous after their long annealing pretreatments. Nonetheless, it seems difficult to describe the sloping plateaux

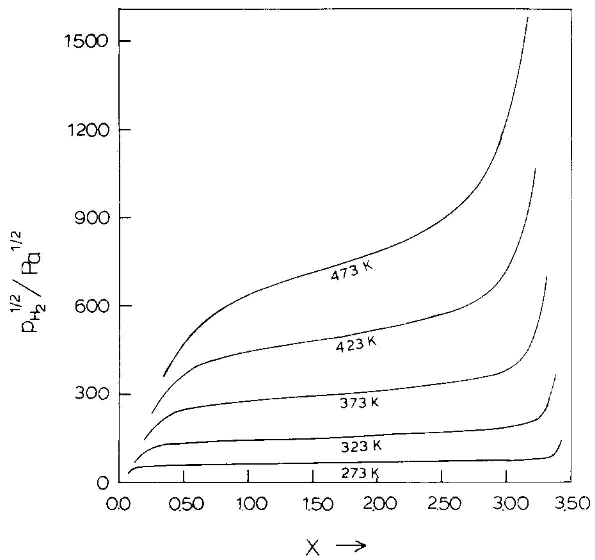

Fig. 10. Calculated sloping plateaux for $ZrMn_2$ at a series of temperatures encompassing the experimental ones shown in Fig. 3. The details of the calculation are discussed in the text.

in any way except by this local model having spreads in the values of $\Delta\mu^{\circ}_{\mathrm{H}}$ and W. It should be noted that the spread in the former quantity for the calculated results shown in Fig. 10 is rather small, corresponding to a compositional variation of $x = 2 \pm 0.05$ judging from the dependence of $\Delta\mu^{\circ}_{\mathrm{H}}$ upon x. This small variation may not arise from any inherent inhomogeneities in the sample but from segregation of one of the components in the vicinity of grain boundaries, etc.

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