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### **The thermodynamics of the LaNi<sub>5</sub>-H<sub>2</sub> system by differential heat flow calorimetry II: the alpha and beta single-phase regions**

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THE THERMODYNAMICS OF THE  $\text{LaNi}_5\text{-H}_2$  SYSTEM BY  
DIFFERENTIAL HEAT FLOW CALORIMETRY  
II: THE  $\alpha$  AND  $\beta$  SINGLE-PHASE REGIONS

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### Summary

Simultaneous pressure-composition isotherms and partial relative molar enthalpies of hydrogen for the single-phase portions of the system  $\text{LaNi}_5\text{H}_x$  with  $0 \leq x \leq 6.4$  were obtained. In absorption the system exhibits chemisorption for  $0 \leq x < 0.05$  with  $|\Delta\bar{H}_\infty^\circ| = 80 \text{ kJ (mol H}_2\text{)}^{-1}$ , followed by trapping for  $0.05 \leq x \leq 0.23$  with  $|\Delta\bar{H}^\circ| = 59 \text{ kJ (mol H}_2\text{)}^{-1}$  at  $x = 0.05$  and then contains an  $\alpha$  solid solution to the phase limit at  $x = 0.42$ . In desorption this phase limit is at  $x = 0.34$ . Both the  $\alpha$ - $(\alpha + \beta)$  and the  $(\alpha + \beta)$ - $\beta$  phase boundaries exhibit discontinuous changes in  $\Delta\bar{H}$  with single-phase  $|\Delta\bar{H}|$  values of  $26.5 \text{ kJ (mol H}_2\text{)}^{-1}$  and  $38.5 \text{ kJ (mol H}_2\text{)}^{-1}$  respectively. The partial relative enthalpy for the  $\beta$  single phase for  $x > 6.05$  decreases slowly with increasing  $x$ .

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### 1. Introduction

Most practical applications of hydrides have used FeTi,  $\text{LaNi}_5$ ,  $\text{Mg}_2\text{Ni}$  and related compounds [1, 2]. Numerous fundamental studies have provided structural, kinetic and mechanistic data [3 - 6]. Thermodynamic data are incomplete. The system  $\text{LaNi}_5\text{-H}_2$  has been chosen for a detailed and complete thermodynamic study using differential twin cell heat flow calorimetry. Whilst  $\text{LaNi}_5$  is not atypical of the group, it does have experimentally attractive characteristics such as easy activation, rapid kinetics, reversibility and moderately low pressure hysteresis, which are not all shared by every member of the group. The present work is an extension of that reported in a previous paper [7] and completes the study of the system with data acquired in the single-phase regions and at the phase boundaries.

### 2. Experimental procedure

The equipment, procedures and results in the two-phase region have been described earlier [7, 8].

Two samples, each approximately 5 g and taken from a 1 kg batch supplied by MPD Technology, Waldwick, NJ, were used. This material was found to be equal in quality to material produced in this laboratory in 3 g quantities from 99.9% pure lanthanum ingot and 99.99% pure nickel foil using dry-box handling and a Centorr argon flow arc melter. The composition was confirmed by wet chemical analysis and atomic absorption analysis to be  $\text{LaNi}_{5.000 \pm 0.010}$ . The purity was determined by using spark source mass spectrometry to be 99.7% metallic (the major impurities being 0.1% Fe and 0.1% Ti) and 99.5% overall (the major non-metallic impurity being 0.2%  $\text{O}_2$ ). Each sample was activated in the calorimeter measurement cell by evacuation to  $5 \times 10^{-7}$  atm followed by pressurization to 35 atm of  $\text{H}_2$  at about 295 K. The samples were fully hydrided and dehydrided three times and all the hydrogen was removed by heating *in vacuo* to 475 K before the calorimetric measurements. At all times after activation the sample was maintained either under hydrogen (Matheson, 99.999% pure) or in a vacuum. Guinier X-ray powder diffraction patterns of the samples showed only reflections assignable to  $\text{LaNi}_5$  and a repeat analysis of one sample after a calorimeter measurement sequence showed no decrease in purity.

All measurements were made with the calorimeter at 285 K. The first sample was cycled in the composition range (of  $\text{LaNi}_5\text{H}_x$ )  $x = 0$  to  $x = 1.05$  and then returned to a composition of about  $x = 0.15$  using a total of 58 simultaneous pressure-composition ( $p$ - $c$ ) and enthalpy measurements. The second sample was cycled in the composition range  $x = 0$  to  $x = 6.4$  and then returned to a composition of about  $x = 0.5$  using a total of 83 measurements. An additional 20 measurements were made with the second sample to confirm details of behaviour in both of the single-phase regions. The changes  $\Delta n$  in hydride composition used in the single-phase regions of approximately 0.12 mmol  $\text{H}_2$  ( $\Delta x = 0.025$ ) were the minimum required for acceptable accuracy (less than  $\pm 2\%$ ). The  $\Delta n$  values used in the  $\alpha + \beta$  coexistence region, approximately 1.0 mmol ( $\Delta x = 0.2$ ), were the maximum changes permissible within the proven linear response range of the calorimeter. Each measurement required between 1.0 - 1.5 h (single-phase regions) and 3.0 - 4.0 h ( $\alpha + \beta$  region). Pressure and thermopile output data were recorded at regular short time intervals. Values of  $q$  were obtained by integrating the thermopile output as described earlier [7]. Baseline parameters were normally chosen from the long-term baseline of a one-day subgrouping of 4 - 7 measurements. In this experimental configuration the enthalpy change  $\Delta h$  corresponding to  $\Delta n$  is given directly by  $q$ ; the  $\Delta n$  values needed to derive  $\Delta \bar{H} = \Delta h / \Delta n$  were obtained as described earlier [7, 8].

### 3. Results and discussion

Figure 1 shows the combined  $p$ - $c$  isotherm and Fig. 2 shows the corresponding  $\Delta \bar{H}$  values for both samples in the  $\alpha$  solid solution and the lower  $x$

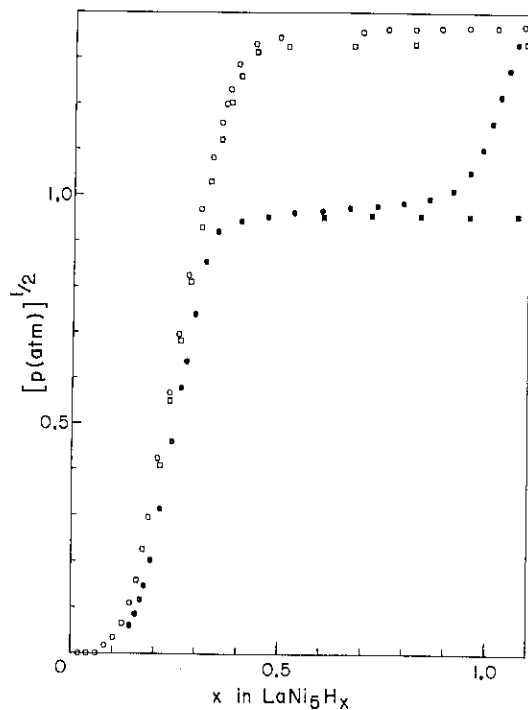


Fig. 1. Pressure isotherms for  $\text{LaNi}_5\text{H}_x$  at 285 K in the composition region  $0 \leq x \leq 1.1$ :  $\circ, \bullet$ , sample 1;  $\square, \blacksquare$ , sample 2 (open symbols are for absorption, full symbols are for desorption). The first 10 absorption points for sample 2 are not shown because they directly overlap results for sample 1.

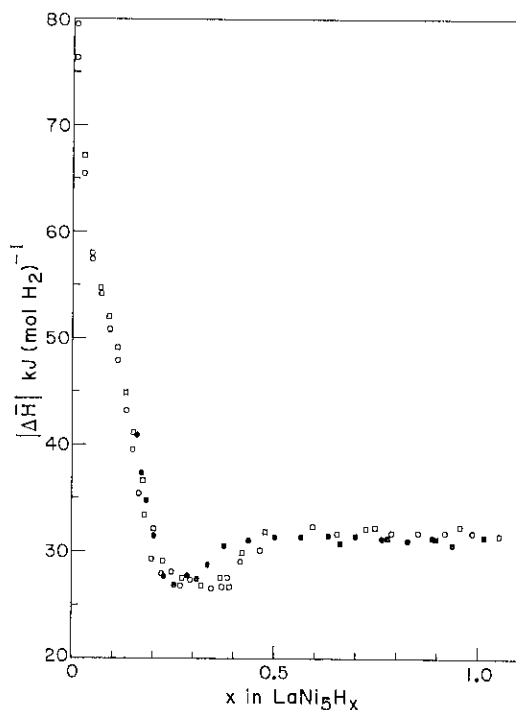


Fig. 2. Absolute partial enthalpies observed in  $\text{LaNi}_5\text{H}_x$  at 285 K for  $0 \leq x \leq 1.1$ . To avoid overlap, five enthalpies are not plotted in the region  $0.15 \leq x \leq 0.35$ . The symbols have the same meaning as for Fig. 1.

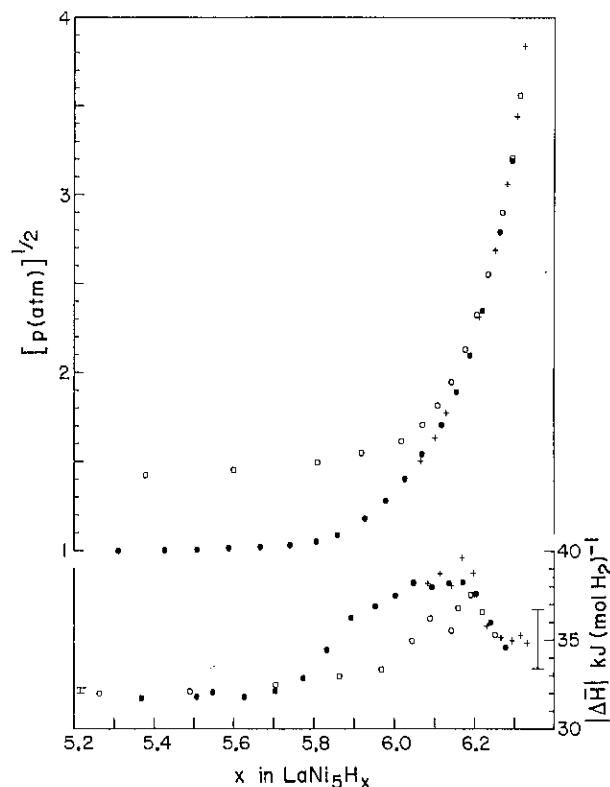
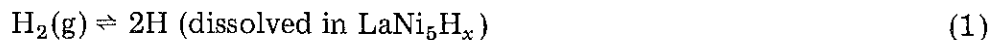


Fig. 3. A combined pressure isotherm and enthalpy diagram for  $\text{LaNi}_5\text{H}_x$  at 285 K in the composition region  $5.2 \leq x \leq 6.4$ : ○, ●, sample 2, main measurement sequence; +, repeat desorption sequence from  $p = 17$  atm. Bars illustrate the errors in the  $\alpha + \beta$  region and at the high pressure end of the  $\beta$  region (recorded in Table 1).

portion of the  $\alpha + \beta$  coexistence region. The  $p$ - $c$  and  $\Delta\bar{H}$  results for the  $\alpha + \beta$  two-phase region, together with a limited number of the results in the single-phase regions, have been given in the previous paper [7]. Figure 3 shows the results for the  $\beta$  single phase and the hydrogen-rich end of the  $\alpha + \beta$  region. Also included in Fig. 3 are a repeat set of desorption measurements using sample 2 and starting at 17 atm of  $\text{H}_2$ .

In the single-phase regions, the  $\Delta\bar{H}$  value measured corresponds to the reaction



where  $x$  is a composition within the single-phase limits. Because  $\Delta n$  is small,  $x$  is virtually constant and  $\Delta\bar{H}$  is approximately the relative partial enthalpy of solution of hydrogen in the hydride of composition  $\text{LaNi}_5\text{H}_x$ .

### 3.1. Isotherm for $0 \leq x \leq 1.1$

The absorption isotherms for the two samples (Fig. 1) showed excellent reproducibility, particularly in the low pressure region (below 0.40 atm). The first three points of both runs ( $x \leq 0.06$ ) showed complete hydrogen ab-

sorption without any hydrogen detectable in the gas phase (pressure less than  $10^{-4}$  atm). This is believed to be due to hydrogen chemisorption. As observed by other researchers [9], the isotherm immediately beyond this chemisorption zone exhibits an immediate deviation from Sieverts' law. In the two-phase coexistence region the absorption pressure  $p_{\text{abs}}$  values obtained using the two samples were in an agreement of 3%, which is remarkable reproducibility for absorption plateau pressures. The initial part of the desorption isotherm for sample 1 from  $x \approx 1.1$  showed the behaviour expected for a scan within the hysteresis loop [10, 11]; pressures approximating the normal desorption isotherm values were attained at  $x \approx 0.9$ . The approach to the desorption pressure  $p_{\text{des}}$  plateau continued until  $x = 0.6$ ; the slope of the  $p_{\text{des}}$  versus  $x$  plot for  $0.6 \leq x \leq 0.9$  is significantly higher than those observed for samples dehydrided from the  $\beta$  phase boundary. In contrast,  $\Delta\bar{H}_{\alpha,\beta}$  values (Fig. 2) agreed with those obtained for desorption from the  $\beta$  phase limit once the major transition to the desorption plateau was complete, *i.e.*  $x < 0.9$ . For sample 1 the desorption isotherm in the  $\alpha$  single-phase region ( $x \leq 0.35$ ) showed a small shift of about 0.015 in  $x$  relative to the absorption isotherm. A similar slightly larger shift was observed for sample 2 [7], which was cycled to higher pressures over a longer time. These shifts are probably the cumulative effects of systematic errors in the measurement of  $\Delta n$  with implied systematic errors of 0.3% to less than 0.1% in each  $\Delta n$  measurement in the single-phase and two-phase regions respectively. The observations are consistent with hydrogen loss due to otherwise undetectable leaks. Another possibility is that these shifts are real, *i.e.* that a small fraction of the absorbed hydrogen is held irreversibly.

### 3.2. Partial enthalpies for $0 \leq x \leq 1.1$

Although the partial enthalpy measurements were made under varying pressure conditions,  $(\delta\Delta\bar{H}/\delta P)_T$  is small and the measured values can be taken as standard relative partial enthalpies  $\Delta\bar{H}_{285^\circ}$  at 285 K. The reproducibility of the partial enthalpies of absorption was within  $\pm 1\%$ . As observed earlier [12], the behaviour of  $\Delta\bar{H}^\circ$  for the  $\alpha$  single phase at low values of  $x$  is markedly different from those of binary hydrides such as Pd-H<sub>2</sub> [13], but shows certain similarities to the behaviour of FeTi-H<sub>2</sub> [14].

The limiting value of  $\Delta\bar{H}^\circ$  ( $\Delta\bar{H}_\infty^\circ$ ) for an infinitely dilute solution of hydrogen was about  $-80 \text{ kJ (mol H}_2\text{)}^{-1}$ .  $\Delta\bar{H}^\circ$  rapidly became less exothermic as  $x$  increases to about  $x = 0.23$ , with a change in slope at about  $x = 0.05$ , the composition at which the first measurable pressure (greater than  $10^{-4}$  atm) also occurred. This rapid decrease in exothermicity of absorption with increasing  $x$  in the  $\alpha$  solubility region (for  $x < 0.23$ ) is the most strikingly anomalous characteristic of these results compared with the behaviour of binary hydrides. In two subsequent measurement sequences with this sample dehydrided at 285 K, limiting  $\Delta\bar{H}^\circ$  values of  $-56.3$  and  $-58.2 \text{ kJ (mol H}_2\text{)}^{-1}$  were obtained; the second value corresponds to a longer evacuation time in the dehydriding process. The  $\Delta\bar{H}$  values from these sequences matched those plotted in Fig. 2 when the  $x$  values were incremented by

0.056 and 0.045 respectively. Bowerman *et al.* [12] have obtained a value  $\Delta\bar{H}_\infty^\circ \approx -56 \text{ kJ (mol H}_2\text{)}^{-1}$  using a sample dehydrided at 298 K. Clearly, the lower dehydriding temperatures leave residual hydrogen in the sample.

The results shown in Fig. 2 are therefore interpreted as follows. For  $x$  less than about 0.05 the hydrogen is chemisorbed with  $\Delta\bar{H}_\infty^\circ = -80 \text{ kJ (mol H}_2\text{)}^{-1}$  and is not removed by the lower temperature dehydriding; such high enthalpies of adsorption, which decrease rapidly with increasing surface coverage, are well known for chemisorbed gases on metals [15] and are consistent with the results of other surface studies [5]. For  $x > 0.05$  the hydrogen dissolves with a limiting partial enthalpy of about  $-59 \text{ kJ (mol H}_2\text{)}^{-1}$ . The change in the nature of the uptake process at about  $x = 0.05$  is also shown by kinetic evidence from pressure and calorimetric data. For  $x < 0.05$ , and particularly for the first measurement ( $\Delta\bar{H} \approx -80 \text{ kJ (mol H}_2\text{)}^{-1}$ ), the pressure indicated complete hydrogen uptake in less than 90 s but the calorimeter data, after correction for the response characteristics, showed a heat effect which continued at measurable rates for about 1.5 h. However, for  $x > 0.05$  there was agreement between sorption rates indicated by the pressure measurements and by the calorimeter output, with the apparent rate (97% complete in 90 s) slightly below that for  $x < 0.05$ .

The ability to monitor very low level reactions using this type of calorimetry provided further information about the nature of the tightly bound hydrogen ( $x < 0.10$ ). During evacuation at 285 K a small endothermic effect occurred ( $330 \mu\text{W}$  after 4 h) which decreased steadily to  $30 \mu\text{W}$  at 72 h (equivalent to  $\delta x/\delta t = -1.8 \times 10^{-3} \text{ h}^{-1}$  and  $\delta x/\delta t = -0.2 \times 10^{-3} \text{ h}^{-1}$ ). This continuing slow reaction indicates that the final desorption rates and the composition attained in lower temperature dehydriding are dependent on the pumping speed at the sample surface, the ratio of the available surface area to the sample weight, and other parameters of the specific system. The endothermic effect stopped within 30 min of closing off the vacuum line, with no measurable pressure increase (less than  $10^{-4} \text{ atm}$ ) in the closed system. The hydrogen sorption at  $x \approx 0.05$  was therefore reversible and the desorbing hydride exhibited an equilibrium pressure of less than  $10^{-4} \text{ atm}$ .

These results, including a sharp change in the slope of the  $\Delta\bar{H}$  versus  $x$  plot at  $x = 0.23$  where  $\Delta\bar{H} = -28 \text{ kJ (mol H}_2\text{)}^{-1}$ , are in good agreement with those reported by Bowerman and coworkers [11, 12] if the  $x$  values of these researchers are incremented by 0.05 to allow for the chemisorbed hydrogen which is not removed by room temperature dehydriding. The observations have been ascribed to trapping in the composition range up to  $x = 0.23$ , with essentially normal  $\alpha$  solid solution behaviour for  $x > 0.23$ . Reilly *et al.* [16] have theorized that, in the region of  $\text{FeTiH}_x$  where behaviour similar to that in this trapping region is exhibited, the hydrogen is absorbed in a structurally perturbed region adjacent to the surface and not as a homogeneous  $\alpha$  solid solution.

In common with binary hydride systems and as predicted by the lattice-gas theory [12], both the absorption and the desorption results exhibited a discontinuity in enthalpy at the upper  $\alpha$  limiting composition. The  $\Delta\bar{H}$

values alone indicate an  $\alpha$  phase limit of  $0.40 \leq x \leq 0.52$  and  $0.31 \leq x \leq 0.44$  in absorption and desorption respectively. More precise estimates can be obtained by also considering the pressure isotherms and the kinetics information derived from the dynamic pressure and calorimeter response curves, since the reaction rate slows by approximately 25% in the  $\alpha + \beta$  region. Using all these sources of information, the best values for the limiting solubilities are  $x = 0.42 \pm 0.02$  (absorption) and  $x = 0.34 \pm 0.03$  (desorption), the second value being regarded as the equilibrium phase limit. The limit in absorption can be compared with the value  $x = 0.50 \pm 0.05$  ( $x = 0.55$  if chemisorption is included) reported by Bowerman *et al.* [12]. It is possible that the thermal history of the sample is responsible for the different  $\alpha$  phase limits in absorption as well as for the variability in reported  $\alpha + \beta$  plateau pressures and the magnitude of the pressure hysteresis [7]. For  $x < 0.34$ , the pressure and enthalpy measurements show that the system is reversible. This is particularly remarkable for  $x \leq 0.23$  where  $|\Delta\bar{H}|$  varies rapidly with  $x$ , since irreversibility was found in the region of similar behaviour in FeTiH<sub>x</sub> [14]. In the FeTi-H<sub>2</sub> system this region is believed to be due to chemisorption.

### 3.3. The region $5.50 < x < 6.40$

This region includes the hydrogen-rich part of the  $\alpha + \beta$  region and the  $\beta$  single-phase region up to an equilibrium pressure of 16 atm. In the main absorption sequence (for sample 2) the final composition was  $x = 6.31$  at  $p = 12.7$  atm, which agrees well with the final composition obtained in this laboratory in several one- or two-step hydridings ( $x = 6.39 \pm 0.02$  at  $p = 21$  atm). This agreement is a further indication of the integrity of the gas titration system [7].

The varying error levels for  $\Delta\bar{H}$  across the entire composition range  $0 < x < 6.4$  are given in Table 1 and illustrated in Fig. 3. It is at the high pressures that the twin cell differential feature of the calorimeter becomes particularly advantageous since no  $V dP$  correction is necessary. The non-ideality correction increases rapidly as the  $\beta$  single-phase region is entered. The cumulative effect on composition, however, is very small and would be of no consequence in  $p$ - $c$ - $T$  measurements. The errors also increase across the  $\beta$  region and originate as follows.

(1) A higher range, lower sensitivity pressure transducer must be used (0 - 17 atm) (*cf.* 0 - 1.7 atm in the  $\alpha$  and  $\alpha + \beta$  regions).

(2)  $\delta x/\delta p$  becomes smaller and therefore pressure measurement errors and minor non-linearities (less than 0.05%) in the transducer response become greater sources of error in  $\Delta n$ . The error due to non-linearity is partially eliminated in the detailed volume calibration procedure [7].

(3) The  $q$  values are smaller so that significant changes result from minor variations in the choices of baselines.

The  $p$ - $c$  and  $\Delta\bar{H}$  results are given in Fig. 3. For desorption from well within the  $\beta$  region,  $\Delta\bar{H}$  increases as the  $\beta$ -( $\alpha + \beta$ ) phase boundary is approached and reaches an apparently constant value of  $38.5 \text{ kJ (mol H}_2\text{)}^{-1}$  for  $6.05 < x < 6.18$ . For  $5.7 < x \leq 6.05$  the enthalpies  $\Delta\bar{H}_{\text{des}}$  of desorption



TABLE 1

Calculated quantities for representative points in the various regions of the LaNi<sub>5</sub>-H<sub>2</sub> system to illustrate error variations

Region	$\rho_{\max}$ ( $\times 10^4$ mol cm <sup>-3</sup> )	$\Delta n_{\text{total}}$ ( $\times 10^3$ mol)	$\Delta n_{\text{gas}}$ ( $\times 10^3$ mol)	$\Delta n_{\text{hydride}}$ ( $\times 10^3$ mol)	Repro- ducibility in $\Delta n_{\text{hydride}}$ (%)	$q$ (J)	Repro- ducibility in $q$ (%)
$\alpha$ ( $x = 0.214$ )	0.0684	0.2895	0.1677	0.1218	0.5	3.922	1.0
$\alpha + \beta$ ( $x = 4.705$ )	0.3958	0.6413	0.0249	0.6164	0.2	19.576	0.2
$\beta$ ( $x = 6.333$ )	6.955	5.152	5.078	0.074	6.0	2.583	1.5
$\beta^a$ ( $x = 6.333$ )	7.096	5.287	5.224	0.063	16 <sup>b</sup>	—	—

The error given for the  $\beta$  region is for the worst case and rapidly diminishes as the  $(\alpha + \beta)$ - $\beta$  boundary is approached.

<sup>a</sup>Calculation assuming ideality.

<sup>b</sup>Error resulting from the ideality assumption.

are intermediate between those of what is taken to be the  $\beta$  phase limit and of the  $\alpha + \beta$  region. This extended region of intermediate  $\Delta\bar{H}$  values is distinctly different from the relatively sharp discontinuity observed at the  $\alpha$ - $(\alpha + \beta)$  boundary. The  $p$ - $c$  curves also show different character at the two boundaries and a good estimate of  $x$  at the  $(\alpha + \beta)$ - $\beta$  boundary from either  $p$ - $c$  or  $\Delta\bar{H}$  data only is impossible. However, the use of  $p$ - $c$ ,  $\Delta\bar{H}$  and qualitative kinetic data, as were used for determining the  $\alpha$  phase limit, yields the best value for the  $(\alpha + \beta)$ - $\beta$  boundary at 285 K as  $x = 6.05 \pm 0.05$  (where  $|\Delta\bar{H}| = 38.5 \pm 0.8$  kJ (mol H<sub>2</sub>)<sup>-1</sup>). The errors quoted are estimates of the total probable error. The  $x$  value obtained for the phase boundary is very close to the stoichiometric composition LaNi<sub>5</sub>H<sub>6</sub> and is possibly significant with respect to interstice occupation factors. For  $x \geq 6.18$ , the absolute enthalpy  $|\Delta\bar{H}_{\text{abs}}|$  of absorption is equal to  $\Delta\bar{H}_{\text{des}}$ , which (in agreement with the  $p$ - $c$  data) indicates reversibility in this region.  $\Delta\bar{H}$  decreases slowly with increasing  $x$  and reaches  $34.8 \pm 1.8$  kJ (mol H<sub>2</sub>)<sup>-1</sup> at  $x = 6.33$  (the error again being the total probable error). Bowerman *et al.* [12] have originally reported a much different  $|\Delta\bar{H}|$ - $x$  behaviour in the  $\beta$  region. However, these workers have obtained additional data using hysteresis loop scans [11, 17] and it is understood that the new results [17] are essentially in agreement with those reported here.

#### 4. Conclusions

There is a great similarity between the pseudobinary system studied here and true binary metal-hydrogen systems. Differences occur mainly in

the dilute hydrogen region where two additional processes are identified in the  $\text{LaNi}_5\text{-H}_2$  system. Chemisorption occurs up to the composition  $\text{LaNi}_5\text{H}_{0.05}$  with the limiting enthalpy  $\Delta\bar{H}_\infty = -80 \text{ kJ (mol H}_2\text{)}^{-1}$ . This is followed by a region up to the composition  $\text{LaNi}_5\text{H}_{0.23}$ , ascribed to hydrogen trapping, during which  $\Delta\bar{H}_{\text{abs}}$  rapidly becomes less exothermic. Beyond this composition the system behaviour is close to that predicted by the mean-field lattice-gas model [12] in that an approximately normal  $\alpha$  solution region with essentially discontinuous increases in  $|\Delta\bar{H}|$  at the phase boundaries, is followed by a decrease in  $|\Delta\bar{H}|$  in the  $\beta$  region. This can be contrasted with at least one binary system,  $\text{Pd-H}_2$ , which does not behave as the model predicts in the  $\beta$  region [13].

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