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THE THERMODYNAMICS OF THE $LaNi_5$–H_2 SYSTEM BY DIFFERENTIAL HEAT FLOW CALORIMETRY
I: TECHNIQUES; THE $\alpha + \beta$ TWO-PHASE REGION

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Summary

The use of a heat flow calorimeter with the differential twin cell configuration to study intermetallic compound–hydrogen reactions is described. The techniques of calibration and operation of both the gas titration system and the calorimeter, which are required to obtain high precision enthalpies, are described and discussed. Enthalpies for the reaction in the two-phase region of the $LaNi_5$–H_2 system are independent of the overall composition but exhibit a small hysteresis with

$$\Delta H_{abs} = -32.30 \pm 0.07 \text{ kJ (mol H}_2)^{-1}$$

$$\Delta H_{des} = 31.83 \pm 0.09 \text{ kJ (mol H}_2)^{-1}$$

where ΔH_{abs} is the enthalpy of absorption, ΔH_{des} is the enthalpy of desorption and the errors are the standard deviations. The value of ΔH_{des} is the best value for the enthalpy of reaction between equilibrium phases with a total probable error of ± 0.5 kJ $(\text{mol H}_2)^{-1}$.

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1. Introduction

Interest in the thermodynamic properties of solid metallic hydrides has increased in recent years primarily because of potential applications of these materials in the energy storage field. There is also a more fundamental interest in such properties since a detailed understanding of the physical chemistry of these systems has not yet been obtained. Most reports have been based on pressure–composition–temperature (p–c–T) measurements on metal–hydrogen or intermetallic compound–hydrogen systems. These generally yield enthalpy values for the two-phase region only, although in many cases detailed p–c–T measurements can be used to derive enthalpies for parts of the solid solution regions [1].

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The combination of a Sieverts p–c–T apparatus with a reaction calorimeter enables direct measurements of Gibbs' free energies and enthalpy changes to be made simultaneously [2 - 4]. This combination also offers a number of other advantages including (1) greater accuracy of enthalpies in the two-phase region, (2) enthalpy values throughout the single-phase regions, (3) the ability to study behaviour at the phase boundaries and (4) the ability to derive reasonably accurate entropies over the entire composition range. In a series of studies at higher temperatures on metal–hydrogen systems, Kleppa and coworkers [2, 5, 6] have illustrated the principles and power of this technique, which has recently been extended to studies of intermetallic compound–hydrogen systems [3, 4]. Here we report the use of a heat flow calorimeter with a differential twin cell configuration to study solid–gas reactions. This experimental arrangement and the use of direct digital control and automated data acquisition have been described previously [7]. Heat flow calorimetry is particularly appropriate for measurements on gas–solid systems because connections to gas manifolds can be readily made such that perturbations in the calorimeter behaviour are relatively minor. The twin cell differential form used here has added benefits for measurements in these systems. The differential thermopile output is less sensitive to minor temperature perturbations in the heat sink than a single cell output is, hence giving better stability and greater precision in heat measurements. The differential measurement also cancels out heat effects due both to $V\,\mathrm{d}P$ effects (especially significant in the higher pressure region) and to heat transfers from the entering gas which is not at the calorimeter temperature.

Free-energy, enthalpy and entropy values for the system $LaNi_5$–H_2 have been obtained. The enthalpy and free-energy results for the $\alpha + \beta$ two-phase region are presented here; results for the α solid solution and the β single-phase region are given in a subsequent paper [8]. The ΔH value obtained in the two-phase region is the enthalpy of reaction of the α phase with hydrogen to form the β phase, often referred to as the enthalpy of formation of the β phase. This value is comparable with that derived from p–c–T measurements in the plateau region and is needed in designing devices for hydrogen storage, compression etc.

2. Equipment

The calorimeter was built by Setaram of Lyon and incorporates two thermopiles, each consisting of 496 chromel–constantan junctions*. It is operable in the range 80 - 475 K using resistance heating and liquid nitrogen for cooling. Details of the theory and characteristics of this type of calorimeter have been given by Calvet and Prat [9], and more recently by

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*The material of the pile junctions was incorrectly identified earlier [7].

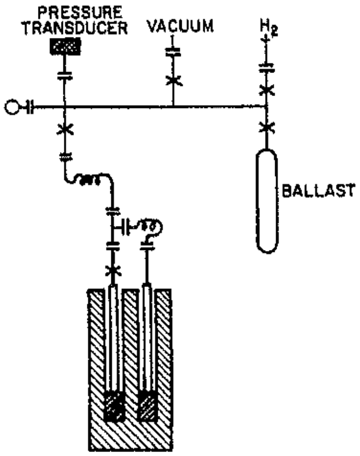

Fig. 1. A schematic diagram of the gas-handling system: =, copper-gasketted vacuum coupling; ×, bellows valve. The vacuum source was a polyphenylether oil diffusion pump.

Gravelle [10]. The calorimeter has a maximum capacity of 15 cm^3 in each measurement zone and for this kind of measurement is operated isothermally (±0.005 K). Details of the operating system, the temperature measurement and control, and the data acquisition and thermopile output amplification and integration etc. are given elsewhere [11, 12]. The operating characteristics have been improved since the previous tabulation [7] as follows: long-term drift in temperature, ±0.005 K in 24 h; pile baseline short-term stability, 0.3 μV; drift over several days, less than 0.5 μV (equivalent to 7 μW).

Detailed attention to the vacuum engineering was essential for the long-term stability and purity of the total amount of hydrogen in the system. For example, the gas-handling system (Fig. 1) was built entirely of 316 stainless steel, using Nupro bellows sealed valves with special Nylon seats. All permanent joints were inert gas welded and disconnections were Cajon VCR fittings using OFHC copper gaskets. The system was leak tight to high vacuum standards (less than 1×10^{-10} standard ml s^{-1}). The calorimeter cells were as shown previously (ref. 7, Fig. 1). An air bath at 301.00 ± 0.05 K surrounded that part of the gas-handling system which was outside the calorimeter. Pressures were measured using a set of all-welded stainless steel capacitance-type pressure transducers with 0.1% accuracy (Setra models 205 with ranges 0 - 1.7, 0 - 6.8 and 0 - 17.0 atm).

3. Calibration and measurement procedure

In this type of calorimetry heat effects are measured as the integral over time of the net differential thermopile signal. The net signal is the measured output minus the small voltage which occurs under zero heat effect conditions (the baseline signal). The sensitivity, usually expressed as μV s mJ^{-1} (equivalent to μV mW^{-1}), is a function of temperature and may be dependent on the experimental arrangement, the power (*i.e.* the rate of heat evolution) and the total heat evolved [10].

The sensitivity was determined to be 72.7 μV s mJ^{-1} by measuring enthalpy increments of α-Al_2O_3 located in the measurement cell and using C_p values reported by Ditmars and Douglas [13, 14]. This was confirmed by $V\,dP$ measurements using hydrogen. The validity of the enthalpy increment calibration procedure was also confirmed and the sensitivity was demonstrated to be independent of the power and/or the total heat effect. A slight dependence of the sensitivity on experimental arrangement was observed, since the value reported here is 3% less than that obtained in other work for calibrating cells which do not have any external connections [12].

The general procedure is to cause a small change Δn in the number of moles of hydrogen in the hydride by the p–c–T gas titration technique [10]. This gives rise to a heat effect q in the calorimeter where

$$q = \Delta h - 0.1013(V' - V_R)\Delta p \qquad (1)$$

and

$$\Delta n = V_D \Delta \rho_D - V_S \Delta \rho_S \pm \Delta a \qquad (2)$$

Equation (1) has been discussed previously [7] and reduces to $q = \Delta h$ when $V' = V_R$. This condition was achieved by placing a quantity of 316 stainless steel rods in the reference cell such that their volume equalled that of the sample in the measurement cell. Equation (2) has also been discussed earlier [7] but is written here in terms of changes $\Delta\rho$ in the gas density, the dosing volume V_D or the system volume V_S. Possible gas absorption and/or desorption on the system walls (Δa) and V_D and V_S values were determined by volume calibration. For most measurements the $\Delta\rho$ values were derived from the measured pressure changes, assuming ideality, but in the β single-phase region corrections for non-ideality were essential.

For the measurements in the two-phase region the reaction was

$$\frac{2}{y-x}\,LaNi_5H_x + H_2(g) \rightleftharpoons \frac{2}{y-x}\,LaNi_5H_y \qquad (3)$$

where x is the upper solubility limit of the α solution and y is the lower solubility limit of the β phase. In this case $\Delta h/\Delta n = \Delta H_{\alpha,\beta}$, the enthalpy of reaction of α phase with one mole of hydrogen to form β phase.

Because the error in Δn was the most serious source of inaccuracy in the enthalpies, particularly in the single-phase regions, careful procedures and calibrations were applied to the acquisition of the p–c data used in eqn. (2). To match the calibration to the measurement system, the reference and sample cells were loaded with stainless steel rods such that in each cell the occupied volume was equal to that of the $LaNi_5$ sample. Hydrogen was expanded to and from the volume V_D with pressure and $\Delta\rho_D$ values identical with those used in the hydride experiments, hence duplicating the conditions of each measurement point. The dosing volume V_D was calibrated by expansions to or from a standard volume which had been determined gravimetrically. The value of V_S was determined by expansion to or from the volume V_D, and since the system was not isothermal this was performed using conditions identical with the measurement conditions. As a result the derived V_S values, calculated assuming the system to be isothermal at the external manifold temperature (301 K), differed slightly from the true system volume. The ratio V_S/V_D is best regarded as an expansion coefficient which is applicable to the particular relative volumes and temperature conditions of the experiment.

Hydrogen was generally used during the calibration, although a few measurements with argon demonstrated the lack of specific gas effects. The value of V_S was reproducible to $\pm 0.2\%$ and was independent of pressure without any hysteresis for final pressures between 0.3 and 6.5 atm. Clearly in this range $\Delta a = 0$. For $p < 0.3$ atm, the value of V_S was pressure dependent and exhibited hysteresis (as a function of the pressure change), probably because of wall adsorption effects. For the range 6.5 atm $< p <$ 17 atm, corresponding to the last few points in the β region of $LaNi_5$ at 285 K, a pressure dependence and hysteresis in the value of V_S (up to 1%) was observed. This is probably due to minor non-linearity and hysteresis in the response of the 0 - 17 atm transducer. A correction for these effects was achieved by the calibration procedure described.

The volume calibration measurements were extended to achieve a calibration of the calorimeter sensitivity which was completely independent of the enthalpy increment procedure described earlier. In the volume calibration configuration $V' = V_R$ and $\Delta h = 0$ so that q should be zero; in practice a very small net pile signal was observed due to small mismatches between the two cells. To achieve a net value of q, a small accurately known volume $V_{cal} \approx 0.7$ cm^3 of the stainless steel rods was removed from the measurement cell and a series of gas expansions was made. A sensitivity was then calculated from the net pile signal and the calculated value of $V_{cal}\Delta p$. These calibrations confirmed the value based on α-Al_2O_3 enthalpy increments to within 0.5% and also showed that the pressure dependence of the sensitivity was probably zero and certainly less than 1% up to 17 atm H_2.

The 5 g $LaNi_5$ sample (analysed as $LaNi_{5.000 \pm 0.010}$) was 99.7% pure considering metallic impurities or 99.5% pure overall [8]. The complete measurement sequence was absorption from $x = 0$ to $x \approx 6.4$ and then desorption to $x \approx 0.5$, *i.e.* still within the $\alpha + \beta$ region. On completion of this cycle, two additional p–c points, without corresponding ΔH measurements, were determined to define the x value of the downward turn in the pressure isotherm. Pressure and q measurements were made for a minimum of 3 h after each hydrogen titration. The Δn values used were approximately 1.0 mmol ($\Delta x \approx 0.2$), producing a q value that was within the proven linear response range of the calorimeter. All measurements were made with the calorimeter at 285 K and the gas-handling system at 301 K.

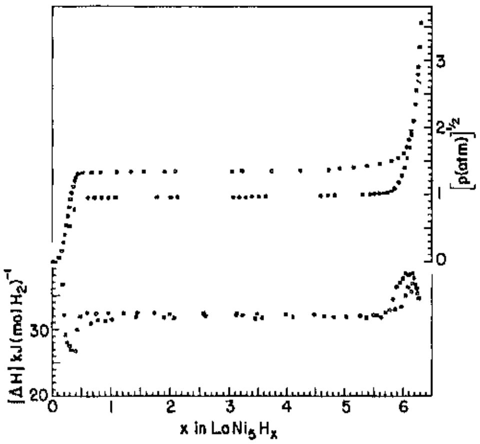

Fig. 2. Enthalpies and pressures in the system $LaNi_5$–H_2 at 285 K: ○, absorption measurements; ●, desorption measurements. p is plotted against the final composition whereas ΔH is plotted against the average composition of each measurement.

4. Results and discussion

Figure 2 shows all the data for the $\alpha + \beta$ region to which eqn. (3) applies ($0.5 < x < 5.50$) together with some of the data for outside this region. The latter data are included solely to give an indication of the behaviour at the phase boundaries and in the single-phase regions; these aspects of the work are discussed in our next paper [8]. Reaction in the $\alpha + \beta$ region was slower than in either of the single-phase regions.

The final two p–c points in Fig. 2 show a small shift in x for the desorption leg in the α region relative to the absorption isotherm. This is probably due to cumulative small (less than 0.5%) systematic errors in the Δn measurements in the single-phase regions (but see also ref. 8).

The results reported here are more precise and accurate than the preliminary results [7] for the following reasons.

(1) The (ten times) larger sample enabled much more accurate determinations of Δn and Δh to be made for the same value of Δx.

(2) The measurements were made with the calorimeter at 285 K, a temperature which lowered the steady state pressures such that all pressure measurements in the α and $\alpha + \beta$ regions could be made with the highest precision (0 - 1.7 atm) transducer. This gave pressure measurements that were reproducible to 2×10^{-4} atm.

(3) With the gas-handling system controlled to ±0.05 K, pressure reproducibility of ±0.02% was possible.

Both the absorption and desorption pressures in the $\alpha + \beta$ region are essentially invariant, which implies good sample homogeneity. In absorption, $p_{abs} = 1.755$ atm at $x = 0.52$ and then the pressure increases uniformly to 1.865 atm at $x = 4.72$, where a more rapid upward drift in p_{abs} begins, and reaches 2.113 atm at $x = 5.60$. This early upward trend in p_{abs} while still apparently in the $\alpha + \beta$ region was also observed by Lundin [15]. For desorption, $p_{des} = 1.010$ atm at $x = 5.7$ and then the pressure decreases uniformly to 0.910 atm at $x = 0.7$. The pressure hysteresis is relatively high: $\ln(p_{abs}/p_{des}) = 0.65$ compared with values of 0.15 - 0.30 found for other samples [7, 15]. Bowerman *et al.* [3] have reported the values $p_{abs} \geqslant 2.78$ atm and $p_{des} = 1.71$ atm at 298 K for $\ln(p_{abs}/p_{des}) = 0.49$. Such wide variability in hysteresis from sample to sample, generally attributable to variations in p_{abs}, is well known in metal–hydrogen systems but the mechanism is uncertain. In contrast, different samples give p_{des} values which are generally reproducible except for variations associated with a composition range in the intermetallic compound [16]. The p_{des} value observed here (0.92 atm for $x = 3.0$) is in good agreement with that predicted from the results of Lundin [15] (0.95 atm at 285 K for $x = 3.0$).

The enthalpy values for both absorption and desorption are independent of x with the following minor exceptions.

(1) In absorption, the $\Delta\bar{H}$ values for the range $4.5 < x < 5.5$ exhibit a decrease (absolute) that is just measurable.

(2) In desorption, a larger decrease occurs as the α phase limit is approached ($0.5 < x < 1.2$).

The region of decrease for the absorption enthalpies corresponds to the region where the pressure begins to increase from the plateau level. Possibly these phenomena are due to minor inhomogeneities in the sample. The small hysteresis in the absolute enthalpies for reaction (3), apparent in Fig. 2, is believed to be real for the following reasons.

(1) The reproducibility of ΔH measurements is particularly high in the two-phase region where the gas system returns to the same pressure after each hydrogen titration. Hence $\Delta\rho_S$ (eqn. (2)) is zero and Δn can be measured with the highest precision. In addition, Δn and q are intentionally made relatively large, so that the overall precision in ΔH is estimated to be ±0.3%.

(2) The detailed volume calibration procedure virtually eliminates the possibility that the difference is due to systematic errors in Δn measurements. In addition, no difference in calorimeter sensitivity between exothermic and endothermic effects was detectable.

Averaging the data in the regions where ΔH is independent of x gives the results designated as average A in Table 1. Seven absorption and five de-

TABLE 1

The enthalpies for the $\alpha + H_2 \rightleftharpoons \beta$ reaction

Average	$-\Delta H_{abs}$ (kJ (mol H_2)$^{-1}$)	ΔH_{des} (kJ (mol H_2)$^{-1}$)
A	32.31 ± 0.07	31.80 ± 0.18
B	32.30 ± 0.07	31.83 ± 0.09

Explanation of the averages is given in the text.

sorption measurements were made using multiple gas titrations for a single q value determination together with long-term (approximately 12 h) baseline monitoring. This yields particularly high precision (±0.2%), giving the average indicated as B in Table 1. Additional measurements for part of the $\alpha + \beta$ region ($0.50 < x < 1.10$) were obtained with another sample [8] and the hysteresis in the $|\Delta H_{\alpha,\beta}|$ value was also observed, with $\Delta H_{\alpha,\beta}$ values in good agreement with those obtained here.

A number of models have been suggested [17, 18] to explain the pressure hysteresis in the $\alpha + \beta$ region. A dislocation mechanism recently discussed by Flanagan *et al.* [18] would apparently be consistent with a ΔH hysteresis in the sense $\Delta H_{des} > |\Delta H_{abs}|$, contrary to the observation made here. The present results, particularly when taken together with $\Delta \bar{S}$ values derived from p–c and enthalpy measurements [19], appear to agree better with the strain mechanism postulated by Lundin and Lynch [17]. The magnitude and sense of the enthalpy hysteresis is as predicted by the behaviour of the relative partial molar enthalpies in the single-phase regions and at the phase boundaries [19].

The value for the enthalpy of formation of the β hydride of $LaNi_5$ (reaction (3)) obtained in this work is -31.8 ± 0.5 kJ (mol H_2)$^{-1}$. Following the usual convention for the sorption sense as the best estimate of equilibrium between stable phases, it is the desorption enthalpy that is quoted. The error is an estimate of the total error, based on 2σ for the highest precision measurements, and includes estimates of calibration uncertainty, pressure transducer non-linearities etc. The result is in good agreement with the various indirect values derived from p–c–T measurements [7] (-30.5 to -32.0 kJ (mol H_2)$^{-1}$) and is just larger than an enthalpy (-30.4 kJ (mol H_2)$^{-1}$) calculated using calorimetric third-law entropies for two compositions, one in each of the α and β single-phase regions [20].

The enthalpy obtained here agrees within error with the preliminary value [7] and with the direct calorimetric value obtained by Hubbard and Connick [21]. These workers used a large sample (50 g) with a composition of $LaNi_{5.000}$ and, at 298 K, they obtained the value -31.6 kJ (mol H_2)$^{-1}$. Finally, the value obtained in the present work is just significantly higher than that (-29.6 ± 1.0 kJ (mol H_2)$^{-1}$ at 298 K) reported by Bowerman *et al.* [3]. The temperature difference between the two measurements is not significant but it is possible that the samples in the two studies differed appreciably in composition. Bowerman *et al.* [3] reported a composition of $LaNi_{5.02 \pm 0.07}$ whereas the sample for the present measurements was $LaNi_{5.000 \pm 0.010}$.

5. Conclusion

Using twin cell differential heat flow calorimetry and extreme care in the construction, calibration and operation of the gas-handling system, a small hysteresis in the absolute enthalpy of the $\alpha \rightleftharpoons \beta$ reaction in the $LaNi_5$–

H_2 system has been detected. The enthalpy of reaction of the α phase with hydrogen to form the β phase is -31.8 ± 0.5 kJ (mol $H_2)^{-1}$ at 285 K.

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