

Low-Temperature Absorption Equilibrium and Chemisorption in the $\text{LaNi}_5(\text{Activated})/\text{H}_2$ System

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Received May 9, 1977

Absorption isotherms for activated LaNi_5/H_2 have been determined in detail at 273 and 195 K. The variation of the two-phase plateau pressure with temperature has been measured from 174 to 273 K and extrapolates well with higher temperature data determined elsewhere; these data yield $\Delta H_{\alpha/\beta} = -15.0$ kJ/mol of H. Hysteresis loops have been examined in the two-phase coexistence region. Excess hydrogen sorption has been determined as a function of the equilibrium hydrogen pressures by differences between sorption by activated and unactivated (low surface area) samples. The enthalpy for the excess sorption has been found to be approximately -30 kJ/mol of H and becomes less exothermic with extent of sorption. The amounts of the excess sorbed hydrogen are larger than anticipated from the measured surface area (BET, krypton, 77.4 K) in order for excess sorption to correspond to chemisorption; nonetheless, arguments are presented to suggest this correspondence.

INTRODUCTION

Pressure-composition-temperature (p-c-T) data have been obtained on the LaNi_5 (activated)/ H_2 system by several workers (1-3). Most emphasis has been placed on the determination of the behavior in the two-phase coexistence region and the maximum hydrogen contents which can be obtained. It is of interest to determine p-c-T data in the primary solubility region, i.e., in the region of solubilities in the intermetallic compound before the hydride phase appears. It is also of interest to extend the p-c-T data to lower temperatures.

The chemisorbed hydrogen, which is in equilibrium with the absorbed hydrogen, is of particular interest with regard to energy (hydrogen) storage because LaNi_5 and other intermetallic compounds of this class, e.g., SmCo_5 , LaCo_5 , are rather remarkable storers of hydrogen. Hydrogen

can be absorbed and desorbed extremely readily (1), and the system is not sensitive to traces of contaminants such as water vapor or CO_2 (4). The chemisorbed intermediate obviously plays a key role in this extreme activity and the characterization of this state might provide useful clues to the desirable features of this compound as a hydrogen storer.

The chemisorbed hydrogen, which is in equilibrium with the dissolved hydrogen, has been characterized on palladium by measuring p-c-T data with palladium black and with a massive sample having a small surface-to-volume ratio (5). The excess sorption by the palladium black compared to the bulk sample represents the chemisorbed hydrogen at a given equilibrium hydrogen pressure. It is planned to employ the same technique for LaNi_5 . Activated LaNi_5 will be used as the high surface area sample and data previously obtained for

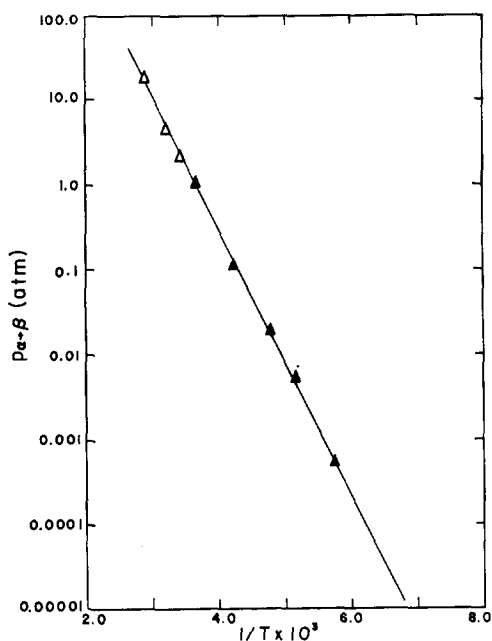


Fig. 1. Plot of two-phase coexistence pressures against $1/T$. (Δ) Data of Ref. (1); (\blacktriangle) present data.

bulk (unactivated) LaNi_5 (β) will be employed for the case in which contributions due to surface chemisorption are minimal.

EXPERIMENTAL

LaNi_5 was prepared by arc-melting the pure elements under an argon atmosphere. The sample was activated within the apparatus to be used for the absorption studies by exposure to ~ 30 atm of hydrogen at 323 K for several hours. The sample was then evacuated and subjected to 30 atm again and was reconverted to the hydride phase. This procedure was repeated 10 times and between each high-pressure treatment the sample was evacuated for 24 hr or longer at 600 K until the pressure fell to $< 10^{-7}$ Torr. Hydrogen pressures were measured with electronic diaphragm gauges (M.K.S. Corp) and recorded with a strip chart recorder so that equilibrium could be established with certainty. The effective volume of the reaction vessel was determined at each temperature by calibration with helium.

The surface area of the sample after 10 cycles of activation was found to be $0.29 \text{ m}^2/\text{g}$ by adsorption of krypton (77.4 K) using the BET method. Van Mal (1) found a value of $0.25 \text{ m}^2/\text{g}$ so the values are in reasonably good agreement.

RESULTS AND DISCUSSION

Pressures over the Two-Phase Coexistence Region

The equilibrium hydrogen pressures over the two-phase coexistence region are shown in Fig. 1 together with data determined at higher temperatures by van Mal (1). The pressures have all been measured in the region of hydrogen content along the two-phase plateau region before they have shown the slight increase due to increase in hydrogen content along the plateau. It can be seen that these low-temperature data on the logarithmic plot line up very well with the higher temperature data of van Mal (1). The heat of absorption corresponding to the temperature dependence of these pressures is -15.0 kJ/mol of H, compared to -15.5 kJ/mol of H found by van Mal and -15.1 kJ/mol of H found by Biris and co-workers (2). The plot of $\ln p_{\alpha/\beta}$ against $1/T$ (Fig. 1) is linear from 0.006 to ~ 20 atm of hydrogen. Such remarkable linearity has also been found in metal/ H_2 systems over broad temperature ranges (7).

Van Mal (1) has suggested that $\Delta p/p$ is constant at different temperatures, where Δp is the pressure difference between the hysteresis loops and p is a two-phase

TABLE 1
Hysteresis Effects in LaNi_5/H_2

Temperature (K)	$p_{\alpha/\beta}$ (Torr)	$p_{\beta/\alpha}$ (Torr)	$\frac{1}{2}RT \ln[p_{\alpha/\beta}/p_{\beta/\alpha}]$ (J/mol of H)	$\Delta p/p_{\alpha/\beta}$
195	3.8	2.5	339	0.34
208	14.1	7.6	436	0.46
273	729	484	464	0.34
313	3,120 (1)	2,430 (1)	325	0.21
353	13,900 (1)	8,800 (1)	320	0.20

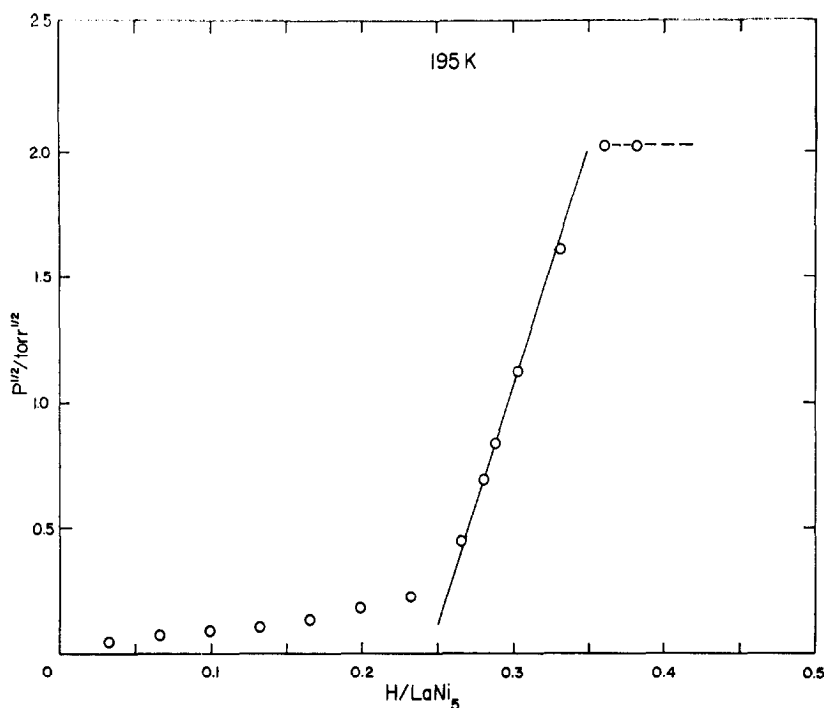


FIG. 2. Absorption data in primary solubility range (195 K).

pressure. Table 1 shows some typical values for the two-phase pressures measured in this research showing hysteresis together with the higher temperature hysteresis data of van Mal (*1*). It can be seen that the function $\frac{1}{2}RT \ln[p_{\alpha/\beta}/p_{\beta/\alpha}]$ is somewhat more constant than is $\Delta p/p_{\alpha/\beta}$, and, furthermore, a rationale can be offered for the constancy of the former function, at least over limited temperature ranges. It can be shown that the energy loss during the hysteresis loop is closely equal to this logarithmic function of pressures (*8*). For palladium/H₂ (*8*) the logarithmic function has values of 840 J/mol of H (273 to 348 K) and decreases at higher temperatures. Therefore, more energy is lost during the hysteresis loops for palladium/H₂ than for LaNi₅/H₂. This may not be unreasonable because palladium retains its massive character following the hydride phase change and therefore it must sustain more plastic deformation during each phase change, whereas LaNi₅ has already disinte-

grated into small particles allowing for relief of most of the strain at the surfaces of the particles despite its larger volume expansion. Wicke and Otto (*10*) have noted a decrease in the value of $\Delta p/p_{\alpha/\beta}$ at 642 K for the two-phase pressure over U/UH₃ in passing from more massive uranium ($\Delta p/p_{\alpha/\beta} = 3.0$) to more finely divided uranium ($\Delta p/p_{\alpha/\beta} = 0.3$), resulting from many cycles of the phase change. These findings support the arguments presented above.

Primary Solubility Region

Data in the primary solubility region are shown at 195 (Fig. 2) and 273 K (Fig. 3). It is apparent that there is an extensive region where the equilibrium pressures are very low. In this region both chemisorption onto the surfaces of the activated sample and solubility in the intermetallic compound must occur. The intersection of the nearly linear portion of the steeply rising pressure region occurs slightly before the

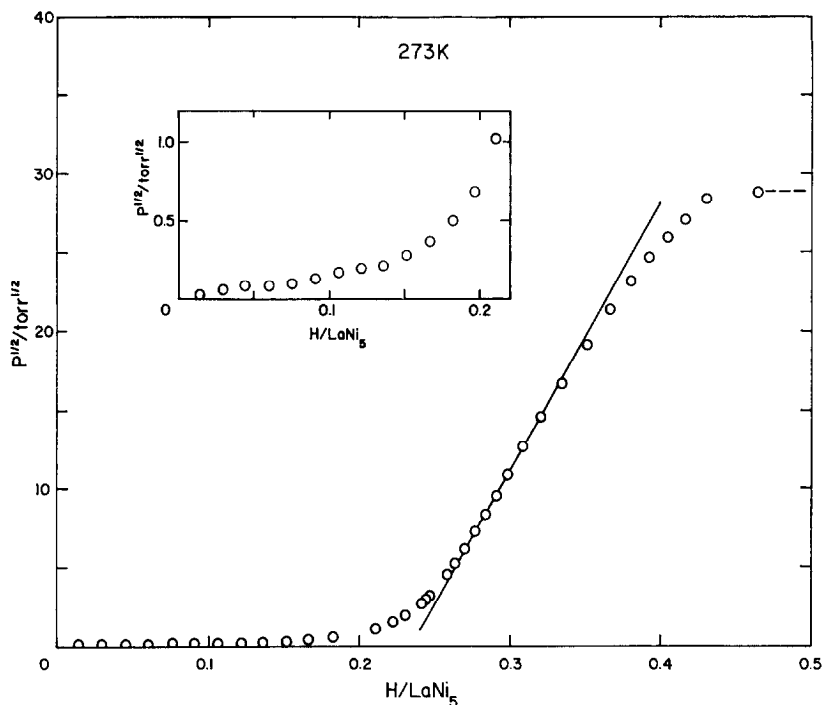


FIG. 3. Absorption data in primary solubility range (273 K). Inset shows low-pressure data in more detail.

appearance of the hydride phase but, nonetheless, approximately reflects the occurrence of hydride formation. Figure 4 shows

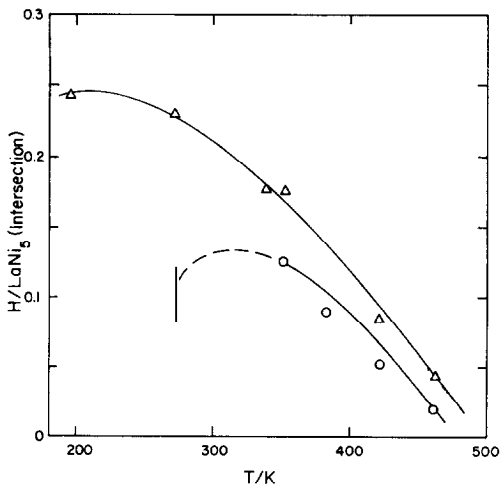


FIG. 4. Plot of intersection of steeply rising portion of isotherms with hydrogen content axis against temperature. (○) Data for unactivated sample (6); vertical line represents approximate value determined here for bulk (unactivated) sample at 273 K; (△) present data for activated sample.

the values of this intersection on the H/LaNi_5 axis where it can be seen that the activated sample has larger values for the intersections than do the bulk samples (6) in the temperature range where data overlap. This is attributed to chemisorption. The values of the intersections first increase and then show a tendency to decrease with decreasing temperature. Equilibrium is very slow in the nonactivated samples and an approximate value for the intersection is shown at 273 K, indicating that the intersection has decreased in this region. The values for the activated samples (Fig. 4) support this decrease with decreasing temperature since it would be expected that more chemisorption should occur at 195 than at 273 K and yet their intersections are quite comparable. This general behavior is quite unusual since for most metal/ H_2 systems the solubility limit in the primary region increases regularly with temperature (9). It suggests that a different type of solution occurs in the low-content

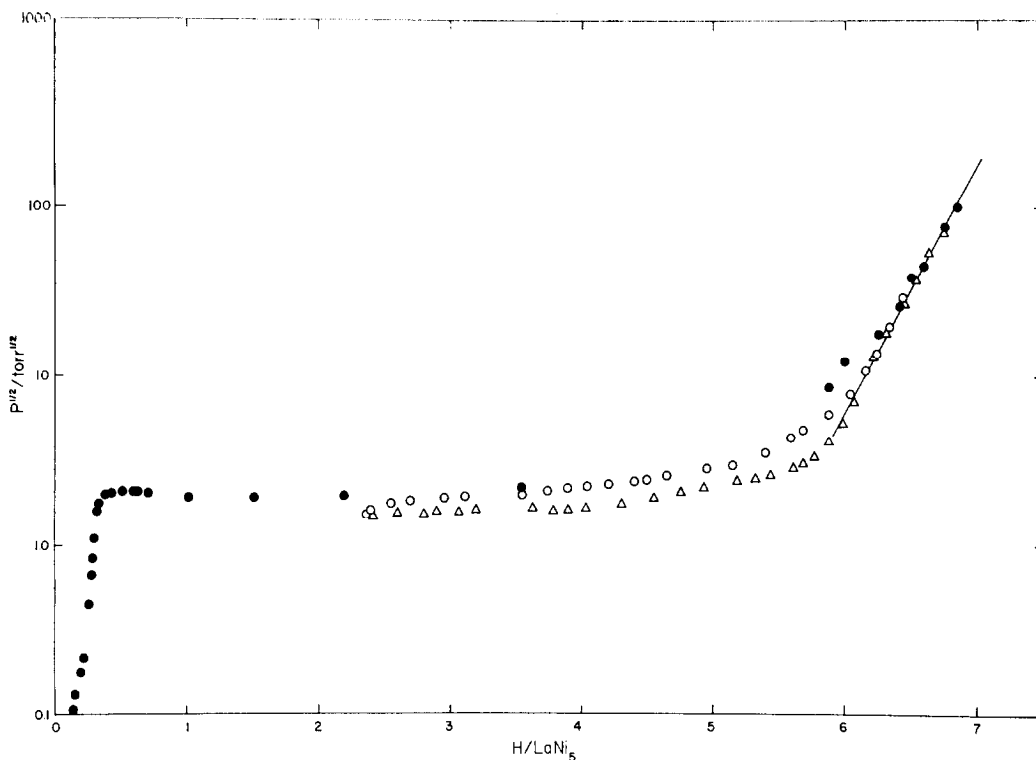


FIG. 5. Absorption isotherm for LaNi₅/H₂ at 195 K. (●) First absorption run after annealing activated sample at 600 K; (Δ) desorption data; (○) reabsorption data.

regions of LaNi₅ than in the regions above the inflection point (Figs. 2 and 3) where the behavior appears more normal.

Absorption (Desorption Isotherms)

Figure 5 illustrates an absorption (desorption) isotherm at 195 K. As observed elsewhere (13) there is a gradual increase in plateau pressures, with H/LaNi₅ increasing during absorption and *vice versa* during desorption. In the region where hydrogen dissolves in the hydride phase, the solubility follows a logarithmic relationship

$$\ln p_{H_2}(\text{atm}) = -43.9 + 6.8 H/\text{LaNi}_5. \quad (1)$$

An equation of exactly the same form has been found for the same region in the palladium/H₂ system (9). This functional relationship results in the palladium/H₂ system from a linear increase of energy of solution of hydrogen with hydrogen content (11, 12).

The nature of the hysteresis is shown in detail in Fig. 6 where it can be seen that finite amounts of hydrogen must be added in order for the system to switch from the desorption to the absorption branch. It is also observed that the original absorption branch always leads to larger pressures than do the subsequent absorptions. This was also noted at 273 K where a hysteresis loop was repeated a second time with no further changes in the absorption branch, i.e., the subsequent absorptions always fell at the same lower pressures than the original one. Prior to these studies the sample had been subjected to hydride formation and decomposition 10 times but between each cycle the sample was annealed at 600 K. Annealing at this temperature may annihilate or reorganize the dislocation network so that the first absorption branch leads to greater plastic deformation than do the subsequent absorptions. The

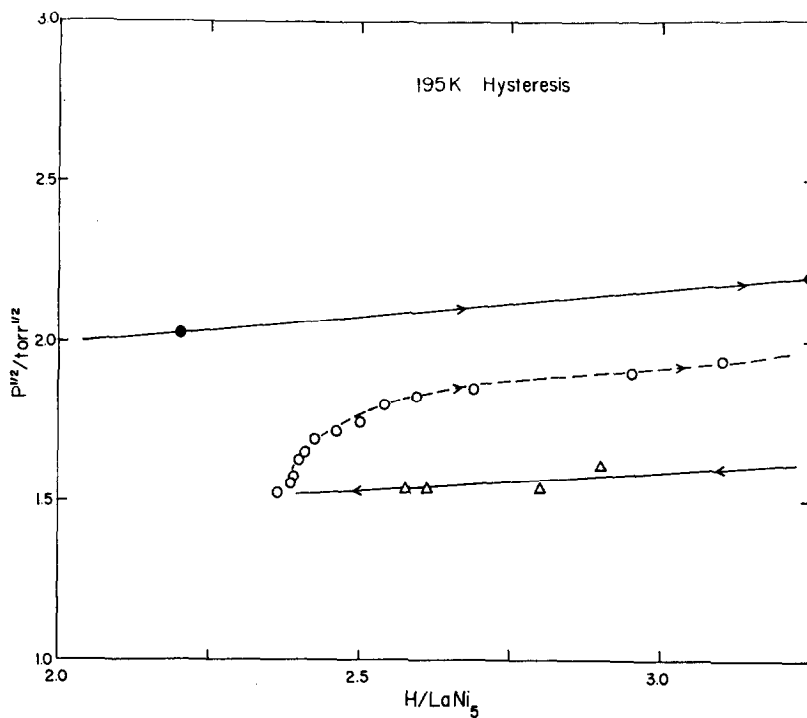


FIG. 6. Details of hysteresis behavior (195 K). (●) First absorption run after annealing activated sample at 600 K; (△) desorption data; (○) reabsorption data.

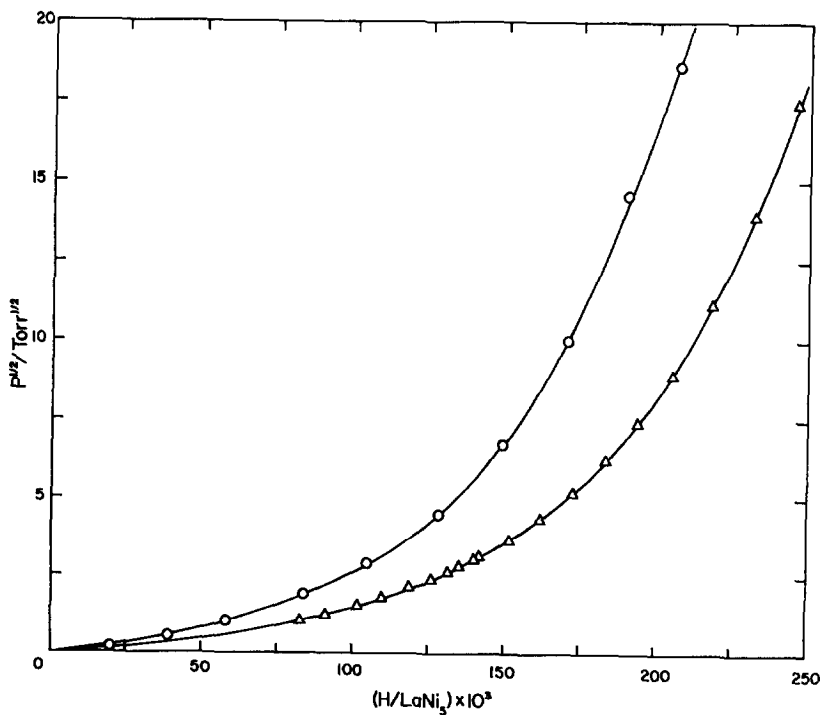


FIG. 7. Absorption isotherms for LaNi_5/H_2 (353 K). (△) Activated sample; (○) unactivated sample (θ).

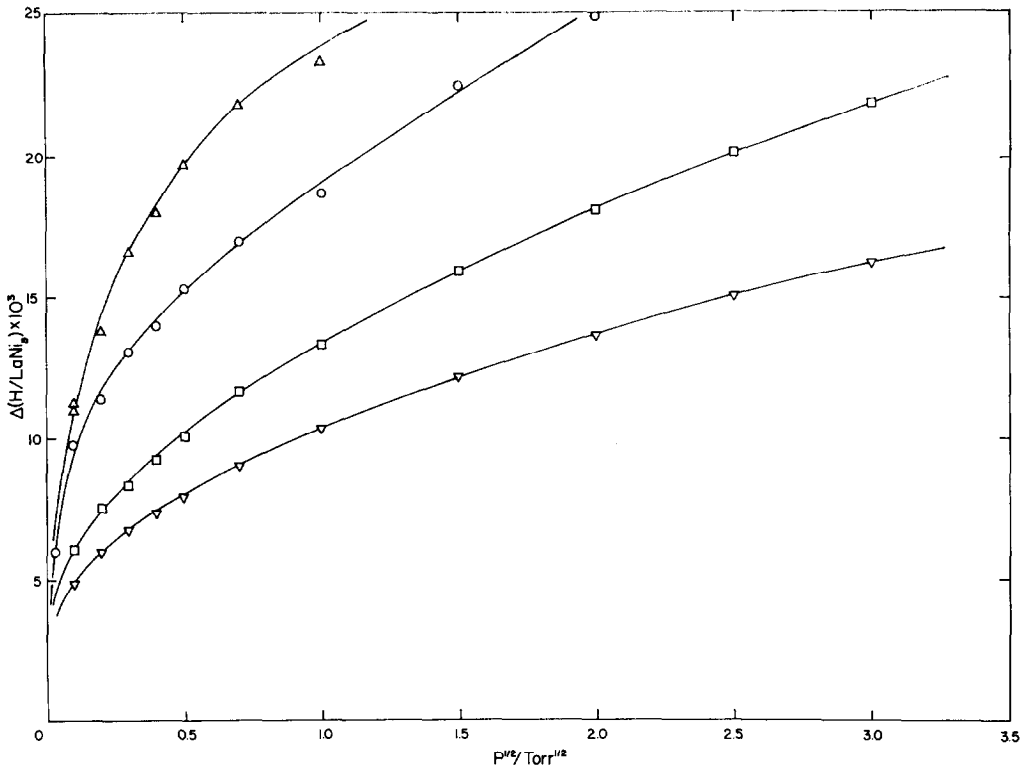


FIG. 8. Excess sorption isotherms for LaNi₅ (activated). (∇) 353 K; (\square) 383 K; (\circ) 423 K; (\triangle) 463 K.

function $\frac{1}{2}RT \ln(p_{\alpha/\beta}p_{\beta/\alpha})$ was determined using absorption pressures after the initial one.

Excess Hydrogen Sorption

Figure 7 shows typical data for activated and bulk samples at 353 K from which excess sorption data have been evaluated. The excess sorption at any equilibrium pressure is determined by differences between the two isotherms. The activated sample was evacuated at 600 K for a prolonged period until the vacuum was $<10^{-7}$ Torr so that it is unlikely that residual hydrogen exists on the surface before initiation of an absorption run. In any case, if residual hydrogen does exist it should not play a role in these measurements since it is strongly held and not in equilibrium with the absorbed hydrogen. The data for the activated sample have been repeated and

are reversible since desorption and absorption data fall onto the same curve. The time for equilibrium to be attained was about 1–2 hr at 353 K.

Differences between sorption by the activated samples and the unactivated samples (low surface area samples) are shown in Fig. 8 as a function of hydrogen pressure. These sorption isotherms closely resemble adsorption isotherms with the coverage tending to level off at higher pressures.

The excess sorption may be reasonably ascribed to either chemisorbed hydrogen or to excess absorption of solute atoms to the tensilely stressed regions about dislocations which are generated during the phase change. The annealing treatment at 600 K should have partially annihilated these dislocations but this is not known for certain. The expected characteristics for dislocation-enhanced absorption can be discerned from the behavior of the palla-

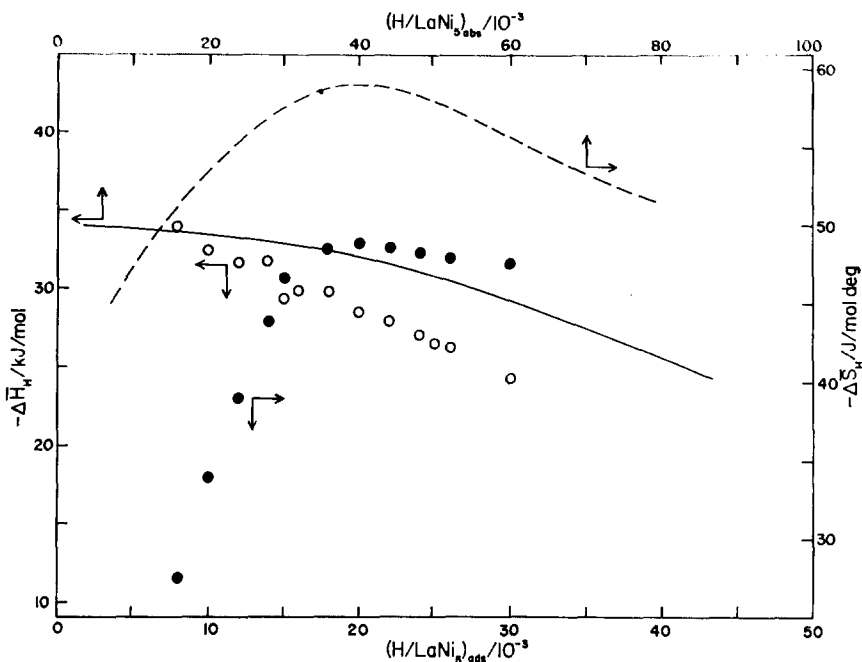


FIG. 9. Plot of $\Delta\bar{H}_H$ and $\Delta\bar{S}_H$ for excess sorption against H/LaNi₅. (○) $\Delta\bar{H}_H$ values; (●) $\Delta\bar{S}_H$ values; continuous curve represents $\Delta\bar{H}_H$ data for unactivated LaNi₅ (6) and broken curve represents $\Delta\bar{S}_H$ for unactivated LaNi₅ (6). An attempt has been made to match the hydrogen contents of the two states of hydrogen so that the data are roughly determined at the same equilibrium pressures.

dium/H₂ system (13-15). It is found for palladium/H₂ that $(H/Pd)^*/(H/Pd)$, where $(H/Pd)^*$ and (H/Pd) refer to the atom ratios with and without a high dislocation density at a given equilibrium pressure, respectively, is unchanged with (H-content) and that the ratio $(H/Pd)^*/(H/Pd)$ decreases with temperature. Both of these trends are expected from the theory of dislocation-enhanced absorption about the stress fields of the edge components of the dislocations (14). For the present data, values of $(H/LaNi_5)^*/(H/LaNi_5)$ decrease with hydrogen content and are nearly unchanged with temperature. This indicates that dislocation-enhanced absorption is not the principal cause of the solubility increases for the activated sample and therefore chemisorption appears to be the most likely source of the excess sorption.

Partial molar enthalpies and entropies for excess sorption (chemisorption) have

been derived from the excess sorption isotherms (Fig. 9). These have been plotted against the excess sorption expressed as $(H/LaNi_5, \text{excess})$ and do not correspond directly with surface coverage. The surface area of the sample has been measured, 0.29 m²/g, and the excess hydrogen corresponds to many times this value if it is assumed that one hydrogen atom is chemisorbed per 10⁻¹⁵ cm² of surface. This indicates that either the true surface area is not being measured by krypton adsorption (77.4 K) or else the interpretation of the excess sorption as mainly chemisorption is erroneous. We prefer the former interpretation and some further evidence to support this is the observation that krypton adsorption was quite slow (1 to 2 hr for the initial dose), indicating slow diffusion into microcracks of the activated sample. It is not unreasonable to expect that small cracks and pores result from mechanical disrup-

tion of the sample accompanying hydride formation. On the other hand, recent transmission electron micrographs (15) do not reveal microcracks in dehydrided LaNi₅; however, these may be extremely difficult to detect since upon expulsion of hydrogen the sample's volume decreases ~25% and the cracks may tend to close to almost molecular dimensions. The observed partial molar enthalpies for the excess sorption are comparable to the value found at infinite dilution for solution of hydrogen in unactivated LaNi₅, i.e., -33.9 kJ/mol of H(6), lending further support for the interpretation of the excess sorption as mainly corresponding to chemisorption since dislocation-enhanced absorption should lead to a greater exothermicity of absorption (14).

CONCLUSIONS

The chemisorbed hydrogen which is in equilibrium with absorbed hydrogen is important because this constitutes the intermediate between the gaseous and adsorbed states. The properties of this hydrogen are related to the nature of the slow step for hydrogen uptake or evolution. If the heat of chemisorption is large compared to the heat of absorption, then there must be an appreciable energy of activation for the transition: chemisorbed state → absorbed state. If, on the other hand, the heat of chemisorption is comparable to the heat of absorption, then an activation energy for the transition may or may not exist. It is suggested that the activation energy for the transition is quite small in this system. Although the heats of the excess sorption (chemisorption) and absorption are comparable in this system, at least over the ranges examined, appreciable chemisorption occurs since the partial entropy for chemisorption is somewhat more positive than for absorption. This may indicate

translational freedom on the surface of the LaNi₅ which is not unexpected in view of the low heats of chemisorption. This mobility may also play a role in the facile uptake and evolution of hydrogen in this system. It appears from these results that desirable energy (hydrogen) storers should have heats of chemisorption comparable to the heats of absorption.

ACKNOWLEDGMENTS

The National Science Foundation is gratefully acknowledged for the financial support of this research.

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