JOURNAL OF SOLID STATE CHEMISTRY 34, 215–221 (1980)

Thermodynamics of Hydrogen Trapping in Intermetallic Compounds: Application to $LaNi_5/H$

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Received July 9, 1979; in revised form August 31, 1979

It has been observed for several intermetallic compound/H systems that deviations from Sieverts' law of ideal solubility occur which are in the opposite direction from the deviations from ideality which occur in pure metal/H systems. The principal source of nonideality on both types of interstitial solutions arises from the changes of the relative partial molar enthalpy of H_2 solution, ΔH_H, with H content. The variations of ΔH_H with H content are, however, in the opposite directions for intermetallic/H and pure metal/H interstitial solutions. Relative partial molar entropies for solution of H_2 in the α-phase of the $LaNi_5/H$ system are given at 298.2 K. These have been determined from calorimetric determinations of ΔH_H and measurements of ΔG_H ($=RT \ln P_{H_2}^{1/2}$). The partial entropies show unusual extrema as a function of H content. A model based on trapping of H atoms is proposed which explains the variations of ΔH_H and ΔS_H. Since the deviations from ideality arising from an increase of ΔH_H with H content seem to be limited to solids with at least two different ordered metal components, e.g., intermetallic compounds, it seems reasonable to assign the trapping sites to interstices which result from an interchange of metal atoms. This interchange may create interstices rich in those nearest-neighbor metal atoms which have the greatest affinity for H.

Introduction

The authors have recently reported a calorimetric investigation of the relative partial enthalpies for H_2 solution in activated $LaNi_5$ (*1*). Activation of the intermetallic compound for hydrogen absorption results from hydride phase formation which is accompanied by a large volume expansion and consequent mechanical disintegration into a finely divided powder. Activated $LaNi_5$ is an excellent hydrogen storage system (*2*). It was found that the enthalpies for H_2 solution increase with n (=H to $LaNi_5$, atom to formula unit ratio) in the α-phase region to $n = 0.23$ and thereafter the enthalpies are relatively invariant with H content to the phase boundary where the hydride phase appears, $n \simeq 0.5$ (298 K) (*1*). The decline in the exothermicity of H_2 solution with n commencing from $n = 0$ must be the principal reason for the initial deviations from Sieverts' law of ideal solubility, i.e., $n = K_s P_{H_2}^{1/2}$, observed in this system (*1, 3, 4*) and other intermetallic systems (*5*) which are in the opposite direction from the deviations noted in pure metal/H systems (*6*). In the latter deviations only commence following a region of solubilities where Sieverts' law is obeyed; by contrast Sieverts' law does not appear to be obeyed even as $n \rightarrow 0$ in the intermetallic H systems. the fact that ΔH_H decreases with n (H to metal atom ratio) for pure metals is well understood (*7*). It reflects the H atom attractive interaction and, below the critical temperature for hydride formation, this leads to the appearance of the hydride phase resulting from hydrogen condensation of the lattice gas. Deviations in

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0022-4596/80/110215-07$02.00/0

Printed in Great Britain

the opposite sense, such as those found for the intermetallic compounds are, at present, unexplained. The purpose of the present paper is to attempt to provide an explanation for such deviations for $LaNi_5/H$; this explanation will presumably be applicable to other intermetallic/H systems as well.

Experimental

The calorimeter has been described elsewhere (*1*). The $LaNi_5$ samples were prepared by arc melting stoichiometric amounts of La and Ni under an argon atmosphere. The resulting button was melted several times to ensure homogeneity. It was then broken into several pieces and 2 to 3 g was used in the calorimeter for a series of runs. The $LaNi_5$ was activated *in situ* in order to avoid exposure of the resulting powder to the atmosphere.

All enthalpies of reaction were determined at 298.2 K and calculated from

$$\Delta H_H = q/\Delta n_H, \qquad (1)$$

where q is the heat due to solution (evolution) of H_2 (g) in (from) the solid and Δn_H is the moles of H dissolved (evolved). The value of q was obtained from

$$q = C_p\Delta T - V_{cal}\Delta p. \qquad (2)$$

Here $C_p\Delta T$ is the measured total heat change, V_{cal} is the gaseous volume of the calorimeter, and Δp is the pressure change within the calorimeter vessel during a run, i.e., $\Delta p = p_{final} - p_{initial}$. V_{cal} was 3.5×10^{-6} m^3. ΔT, of course, depended upon the size of the dose of H_2, but for a typical run the temperature change was 0.01 K. This corresponded to a pressure change of approximately 6.7×10^4 Pa and a change in $H/LaNi_5$ of approximately 0.04 or 3×10^{-4} moles of H absorbed. The correction term, $V_{cal}\Delta p$, reduces the measured heat change typically by 5 to 10% for both absorption and desorption calorimetric runs.

H_2 pressures were recorded with a M.K.S. diaphragm gauge (0 to 1.33×10^6 Pa) that gave readings to the nearest 1.33×10^2 Pa for $p > 1.33 \times 10^5$ Pa and to 1.33×10 Pa for $p < 1.33 \times 10^5$ Pa. Equilibrium could be determined unambiguously by the use of a strip chart recorder. Δn_H was calculated from the pressure changes within the known volumes employing the ideal gas law. The heats of reaction were reproducible to within ±1 kJ/mole H.

Results and Discussion

The reaction investigated is described by

$$\tfrac{1}{2}H_2(g) \rightleftarrows H(\text{dissolved in } LaNi_5H_x), \qquad (3)$$

where x is less than 0.5 for α-phase $LaNi_5/H$ and x does not change significantly during a calorimetric determination, i.e., the heat changes closely approximate partial molar enthalpies. Results are shown in Fig. 1. Both absorption and desorption data give the same results. Concomitant measurements of the equilibrium H_2 pressures as a function of

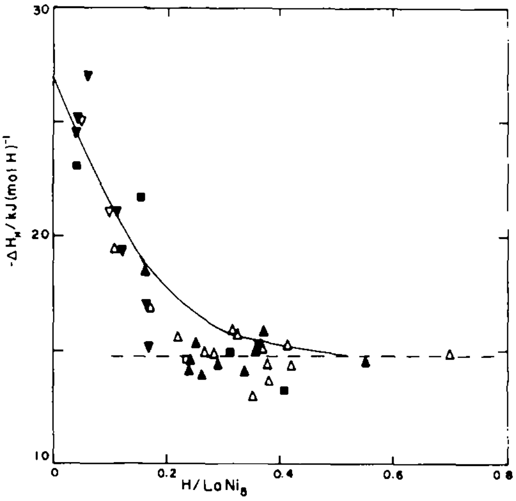

FIG. 1. Plot of ΔH_H against $H/LaNi_5$, atom to formula unit ratio (298.2 K). ▽, □, and △ represent three different samples. Filled symbols are for absorption and open symbols for desorption runs. – – –, ΔH for the two (solid)-phase reaction; ——, calculated from Eq. (11).

n give the relative partial molar Gibbs free energy for reaction (3) with respect to a standard state of $P_{H_2} = 1$ atm,

$$\Delta G_H = RT \ln P_{H_2}^{1/2}, \qquad (4)$$

and the combination of the calorimetrically determined enthalpies and partial molar free energies gives the relative partial molar entropies which correspond to reaction (3) with $P_{H_2} = 1$ atm. (The enthalpies are measured for various H_2 pressures but this does not affect their values because ΔH_H is independent of P_{H_2} at least for the small pressures employed here; however, ΔG_H and ΔS_H refer to 1 atm H_2.) Figure 2 shows the equilibrium H_2 pressures in the α-phase region at 298.2 K. Using Eq. (4) and $\Delta S_H = (\Delta H_H - \Delta G_H)/T$ values of ΔS_H have been derived and their rather strange dependence upon n is shown in Fig. 3 (298.2 K).

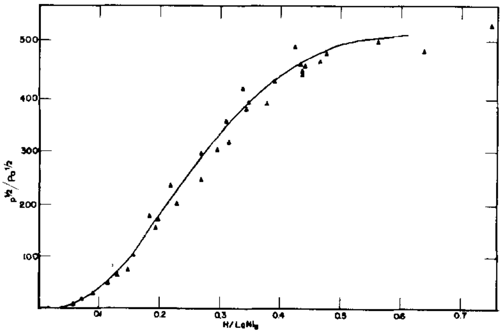

FIG. 2. Plot of $P^{1/2}$ versus H/LaNi5 at 298.2 K. △, experimental data from several runs; continuous curve used to calculate $\Delta G_H = RT \ln P_{H_2}^{1/2}$.

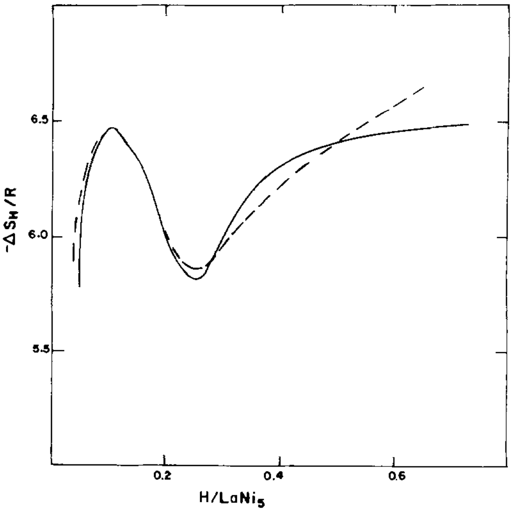

FIG. 3. Plot of $\Delta S_H/R$ versus H/LaNi5, atom to formula unit ratio (298.2 K). ——, experimental curve derived from best fit of ΔH_H values and from plot of $P_{H_2}^{1/2}$ versus H/LaNi5. - - -, calculated from Eqs. (12) and (13).

It is suggested here that the intial decrease of exothermicity of H_2 solution in LaNi5 (Fig. 1), and in intermetallic compounds in general (*5*), is due to progressive filling of traps. These traps have a greater affinity for H than do the normal interstices. Since pure metal/H systems show the opposite trend for the dependence of ΔH_H upon n, it seems reasonable to conclude that the traps must be in some way associated with intermetallic structures and therefore the traps do not correspond to metal atom vacancies, interstitials, or other defects which would be common to both metals and intermetallic compounds. This leads one to conclude that the trapping sites most probably arise from the imperfect nature of the intermetallic structures, i.e., metal atoms in wrong positions. For the case of LaNi5, some La and Ni atoms are assumed to be interchanged leading to interstices which are especially rich in La nearest neighbors. Surface segregation observed by Schlapbach *et al.* (*8*) may be a source of such defects, i.e., they have found that the surface La:Ni ratio is 1 : 1 rather than 1 : 5; the bulk ratio is only found after sputtering away 50 Å of surface. In this 50 Å layer there must be many interstices which are rich in La nearest neighbors. If it is assumed that the same circumstance holds for the activated small particles, then 0.75% of the material is defective since the average particle size is 4×10^{-6} m (*2*). There are three interstitial sites (D1 sites) in LaNi5 which are occupied in the α-phase (*9, 10*). If it is assumed that, on an average, these all become trapping sites in the defective 50 Å layer adjacent to the surface, then 2.2% of the D1 sites are trapping sites. In the trapping model derived below, it is estimated that 5% of the D1 sites are trapping sites. It may be that the trapping sites in $LaNi_5$ do not arise from surface segregation since there are also expected to be bulk sites which may be defective because of the finite thermodynamic concentration of atoms in wrong positions; however, the above argument demonstrates that surface segregation *could* give rise to traps in about the correct order-of-magnitude concentration.

The Trapping model

Many authors have considered the effect of trapping sites on interstitial solution properties (*11–13*). The goal of the present model is somewhat more ambitious than that of previous contributions, i.e., our goal is to compare the predictions of the model with experimental partial thermodynamic parameters over a wide range of α-phase H contents. The model is independent of the origin of the traps. The following treatment commences from the model given by Pfeiffer and Wipf (*12*). It is assumed that there are n_t moles of trapped H and n_f moles of free H, i.e., interstitially dissolved H in normal interstices; L is the moles of $LaNi_5$, N_f is the moles of free sites, and N_t is the moles of trapping sites. β_t and β_f are defined by $N_t = \beta_t L$ and $N_f = \beta_f L$. Only one type of trap is assumed to exist and the energy of the trap relative to a free interstitial site is ε per mole H and we assume, following Pfeiffer and Wipf (*12*), that $S°_H$ is the same in the traps and free sites, where $S°_H$ is the excess entropy as $n \to 0$.

The chemical potential of the trapped H atoms is given by

$$\mu_H^t = \varepsilon + RT \ln\left(\frac{n_t/N_t}{1-(n_t/N_t)}\right) = \varepsilon + RT \ln\left(\frac{\theta_t}{1-\theta_t}\right) \qquad (5)$$

and free H atoms

$$\mu_H^f = RT \ln\left(\frac{n_f/N_f}{1-(n_f/N_f)}\right) = RT \ln\left(\frac{\theta_f}{1-\theta_f}\right), \qquad (6)$$

where H–H interactions have been omitted; this is not unreasonable because there is no evidence for H–H interactions in the region of H contents after the traps have been fiilled, i.e., $n > 0.23$ (Fig. 1). Although each trap could trap more than one H, this is not likely. The most likely possibility is that a La atom in the wrong position might create more than one trap, each one of which can be occupied by one H. It is also assumed that there are no blocking effects, i.e., occupation of one trap will not block adjacent traps for H occupation. At equilibrium $\mu_H^t = \mu_H^f$ and therefore

$$n_t/N_t = \frac{n_f/N_f}{n_f/N_f[1-\exp(\varepsilon/RT)] + \exp(\varepsilon/RT)} \qquad (7)$$

and

$$\frac{n_t + n_f}{L} = n_H/L = n. \qquad (8)$$

Solving Eqs. (7) and (8) simultaneously we obtain

$$\frac{n_t}{L} = f_t n = (1 - f_f)n$$

$$= \frac{\beta_f e^{\varepsilon/RT} + \beta_t + n(1-e^{\varepsilon/RT}) \pm \{[\beta_f e^{\varepsilon/RT} + \beta_t + n(1-e^{\varepsilon/RT})]^2 - 4n\beta_t(1-e^{\varepsilon/RT})\}^{1/2}}{2(1-e^{\varepsilon/RT})}. \qquad (9)$$

f_t is defined by Eq. (9) and represents the fraction of H in the traps at any value of n; f_f is also defined by Eq. (9) and it is the fraction of H in the free sites. (The negative sign in front of the square-root term gives physically meaningful results and the positive sign does not.)

Another quantity of interset is $(\partial(n_t/L)/\partial n)_{T,p}$ which is a measure of how the trapped H concentration changes with the total H concentration. This is obtained by differentiation of Eq. (9) with respect to n,

$$\begin{aligned}(\partial n_{\mathrm{t}}/\partial n_{\mathrm{H}})_{T,p} &= (\partial(n_{\mathrm{t}}/L)/\partial n)_{T,p} = f_{\mathrm{t}}^{*} = 1 - f_{\mathrm{f}}^{*} \\ &= \frac{1}{2}\left[1 - \frac{\beta_{\mathrm{f}}\, e^{\varepsilon/RT} + n(1-e^{\varepsilon/RT}) - \beta_{\mathrm{t}}}{\{[\beta_{\mathrm{f}}\, e^{\varepsilon/RT} + \beta_{\mathrm{t}} + n(1-e^{\varepsilon/RT})]^2 - 4\beta_{\mathrm{t}}(1-e^{\varepsilon/RT})\}^{1/2}}\right], \quad (10)\end{aligned}$$

where f_{t}^{*} and f_{f}^{*} are defined by Eq. (10) and refer to the fraction of H atoms entering the traps and free sites, respectively at a given value of n. The fractions without asterisks are needed for calculation of integral thermodynamic parameters. The fractions marked with asterisks are needed for the calculation of the partial thermodynamic parameters, i.e.,

$$\Delta H_{\mathrm{H}} = f_{\mathrm{t}}^{*}\, \Delta H_{\mathrm{H}}^{\mathrm{t}} + f_{\mathrm{f}}^{*}\, \Delta H_{\mathrm{H}}^{\mathrm{f}}, \quad (11)$$

$$-S_{\mathrm{H}}^{\mathrm{c}}/R = f_{\mathrm{t}}^{*} \ln\left(\frac{n_{\mathrm{t}}/L}{\beta_{\mathrm{t}} - n_{\mathrm{t}}/L}\right) + f_{\mathrm{f}}^{*} \ln\left(\frac{n_{\mathrm{f}}/L}{\beta_{\mathrm{f}} - n_{\mathrm{f}}/L}\right), \quad (12)$$

where $S_{\mathrm{H}}^{\mathrm{c}}$ is the partial configurational entropy of dissolved H.

Application of the Trapping Model to $\mathrm{LaNi_5}$

In order to be able to calculate the various fractions and hence the partial thermodynamic quantities, values must be assigned to β_{f}, β_{t}, and ε. These have been chosen to be commensurate with experiment, i.e., they are not adjustable parameters. β_{f} is known to be 3 since the D1 sites are occupied in the α-phase of $\mathrm{LaNi_5}$ (*9*) and there are three of these sites per formula unit of $\mathrm{LaNi_5}$. ε is taken as 12 kJ(mole H)$^{-1}$ which corresponds to the difference in values of ΔH_{H} at $n = 0$ (−26.8 kJ(mole H)$^{-1}$) (Fig. 1) and the value (−14.8 kJ(mole H)$^{-1}$ in the region of H contents where the traps appear to be filled, i.e., $n > 0.23$ (Fig. 1). β_{t} is the most adjustable of these parameters but it must lie within the range $n = 0$ to 0.23 and the best agreement is obtained with $\beta_{\mathrm{t}} = 0.15$ (small variations in β_{t} (10 to 15%) do not make much difference in the degree of fit of the calculated to the experimental results). Table I shows the results of the model calculations, where ΔH_{H} is calculated from Eq. (11) using the following values: $\Delta H_{\mathrm{H}}^{\mathrm{t}} = \Delta H^{\circ}{}_{\mathrm{H}} =$ −26.8 kJ(mole H)$^{-1}$ and $\Delta H_{\mathrm{H}}^{\mathrm{f}} =$ −14.8 kJ(mole H)$^{-1}$ (Fig. 1). The agreement of the calculated values with the experimental values is shown in Fig. 1 and it can be seen that the experimental trend is reproduced well. The calculated values asymptotically approach the value of $\Delta H_{\mathrm{H}}^{\mathrm{f}}$ whereas the experimental values appear invariant for $n > 0.23$ but this is within the experimental error of ±1 kJ(mole H)$^{-1}$.

In order to compare the calculated partial entropies to the experimental values the other contributions to the entropy of solution must be added to the configurational term, i.e.,

$$\Delta S_{\mathrm{H}} = S_{\mathrm{H}}^{\mathrm{c}} + S^{\circ}{}_{\mathrm{H}} - \tfrac{1}{2} S^{\circ}{}_{\mathrm{H_2}}, \quad (13)$$

where ΔS_{H} is the relative partial molar entropy of solution. It is assumed that $\Delta S^{\circ}{}_{\mathrm{H}} = S^{\circ}{}_{\mathrm{H}} - \tfrac{1}{2} S^{\circ}{}_{\mathrm{H_2}}$ is independent of n and the choice of $\Delta S^{\circ}{}_{\mathrm{H}}/R = -8.3$ (selected to give a correspondence with experimental data at the minimum in Fig. 3) gives the

TABLE I

CALCULATED VALUES OF ΔH_{H} AND $S_{\mathrm{H}}^{\mathrm{c}}$ VIA EQS. (12) AND (13) WITH $\beta_{\mathrm{t}} = 0.15$, $\beta_{\mathrm{f}} = 3.0$, AND $\varepsilon = -12.0$ kJ(mole H)$^{-1}$ (298.2 K)

n	n_{t}/L	f_{t}	f_{t}^{*}	$S_{\mathrm{H}}^{\mathrm{c}}/R$	ΔH_{H}/kJ (mole H)$^{-1}$
0.05	0.0408	0.816	0.770	2.08	−24.0
0.10	0.0754	0.754	0.611	1.86	−22.1
0.20	0.1166	0.583	0.241	2.39	−17.7
0.25	0.1258	0.503	0.143	2.47	−16.5
0.30	0.1315	0.438	0.090	2.39	−15.9
0.40	0.1348	0.337	0.050	2.11	−15.4
0.50	0.1408	0.282	0.024	1.88	−15.1

TABLE II

CALCULATED TRAP OCCUPATION FRACTIONS AND PARTIAL THERMODYNAMIC PARAMETERS FOR $n = 0.10$ AT VARIOUS TEMPERATURES

($\beta_t = 0.15$, $\beta_f = 3.0$, AND $\varepsilon = -12$ kJ (mole H)$^{-1}$)

	273 K	298 K	323 K	373 K	423 K	463 K
f_t	0.818	0.754	0.701	0.594	0.505	0.447
f_t^*	0.673	0.611	0.558	0.527	0.408	0.366
$\Delta H_H/R$	−2.752	−2.662	−2.585	−2.540	−2.368	−2.308
S_H^c/R	1.54	1.86	2.11	2.25	2.70	2.83

results shown in Fig. 3. The most unusual aspects of the experimental data, i.e., the extrema, are seen to be reproduced quite well by the trapping model and therefore the model is judged to be successful.

Consequences of the Trapping Model

It is predicted from the trapping model that the fraction of H in traps (Eq. (9)) at a given value of n decreases with temperature and also that the fraction of H entering the traps at a given n value decreases with temperature. This will cause the values of both ΔH_H and S_H^c to increase with temperature. Tanaka and Flanagan have determined from pressure–composition–temperature (p–c–T) data values of ΔH_H and ΔS_H for unactivated $LaNi_5$ where this trend was noted (*3*). Neumann (*4*) also observed the same trends. For an arbitrary small H content we have calculated how the fractions and partial thermodynamic parameters change with temperature (Table II).

It can be seen that the partial thermodynamic parameters exhibit a considerable temperature dependence, e.g., $S_H^c = 12.80$ J(K mole H)$^{-1}$ at 273 K and 23.52 J(K mole H)$^{-1}$ at 463 K. This change arises entirely from configurational changes due to redistribution of the population of H between the traps and free sites.

p–c–T data will, in principle, yield the correct values of ΔH_H and ΔS_H at any one temperature; it should be stressed that these quantities are more strongly temperature dependent when traps are present than in their absence and therefore detailed p–c–T data are required in order to determine accurate values of these partial thermodynamic quantities whereas at a given temperature the calorimetric–equilibrium H_2 pressure method is accurate and is therefore better suited for the determination of these quantities.

Acknowledgment

The authors wish to thank the National Science Foundation for financial support.

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