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Hydrogen solution in homogeneous Pd–Fe alloys

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Abstract

Thermodynamic properties for H_2 solution and hydride formation in Pd–Fe alloys have been determined from pressure–composition isotherms and from reaction calorimetry. The dilute phase solubility in the Pd–Fe alloys appears to be anomalous because the Sieverts' constants for $X_{Fe} \geq 0.0374$ do not extrapolate linearly to the value for pure Pd–H. Substitution of Fe in the Pd lattice causes the unit cell size to decrease and thus this system is contracted with respect to Pd. Contracted Pd-rich alloys generally have increased plateau pressures as compared to Pd and the Pd–Fe alloys are no exception. Enthalpies for the plateau reaction have been determined by both p–c–T and reaction calorimetric methods. The enthalpy magnitudes decrease with atom fraction Fe from 19.1 kJ/mol $\frac{1}{2}H_2$ ($X_{Fe}=0$) to 13.5 ($X_{Fe}=0.10$) as determined from reaction calorimetry.

Keywords: Hydrogen solubility; Pd/Fe alloys; Thermodynamics

1. Introduction

Hydrogen solubilities have been measured in 46 different fcc binary Pd-rich alloys and several of these systems have been measured many times. For example, there are more than six papers on the (Pd+Ag+H) system, however, there is only one paper on the thermodynamics of H_2 absorption by Pd–Fe alloys [1] despite the importance of Fe itself.

The lattice parameters of fcc Pd–Fe alloys have been shown to decrease with increase of X_{Fe} [1–4]. Thus the Pd–Fe alloys fall into the category of ''contracted'' alloys because their unit cells are smaller than Pd. The decrease of lattice parameter with X_{Fe} is more marked than the analogous decrease in the closely-related Pd–Co system [5].

Contracted Pd alloys generally interact less exothermically with H_2 than Pd. This is consistent with the observation that these Pd–Fe alloys are found to dissolve H_2 less exothermically than Pd in the dilute phase [1]. Data are not available for thermodynamic parameters for the two phase plateau region of the Pd–Fe alloy–H systems and these will be determined in this research.

2. Experimental

Substitutional Pd-alloys were prepared by arc-melting the pure elements under argon. The buttons were flipped and re-melted several times. They were then annealed in vacuo for 3 days (1133 K), rolled into foil and then re-annealed for 2 days (1133 K) before the thermodynamic measurements were carried out. In this research thermodynamic parameters for H_2 absorption and desorption were determined from H_2 pressure–composition isotherms and enthalpies of H_2 solution were determined calorimetrically. In the calorimetric determinations δn_H mols of H were added or removed from the alloy where δn_H was small so that the measurements were carried out at nearly constant $H/M=r$, $(\delta q/\delta n_H)_r \approx \Delta H_H$ where δq is measured in a dual-cell, heat-leak calorimeter described elsewhere [6] and ΔH_H is the relative partial molar enthalpy for hydrogen solution.

3. Results and discussion

3.1. Dilute phase solubilities

Some dilute phase solubilities determined here are shown in Fig. 1 (323 K). The H_2 solubilities appear to be independent of X_{Fe} in the range from 0.0 to 0.018 because all of these data can be nearly superimposed on the solubility relationship for Pd–H (Fig. 1). For alloys with $X_{Fe} \geq 0.037$, a decrease in H_2 solubilities with X_{Fe} can be clearly seen. If the Sieverts' plot slopes, $K_s = \left(r/p_{H_2}^{1/2}\right)_{r\to 0}$ where $r=H/M$, are plotted as a function of X_{Fe}, they do not linearly extrapolate to the value for pure Pd–H (Fig. 2). Data for the Pd–Co–H system are also shown [7]

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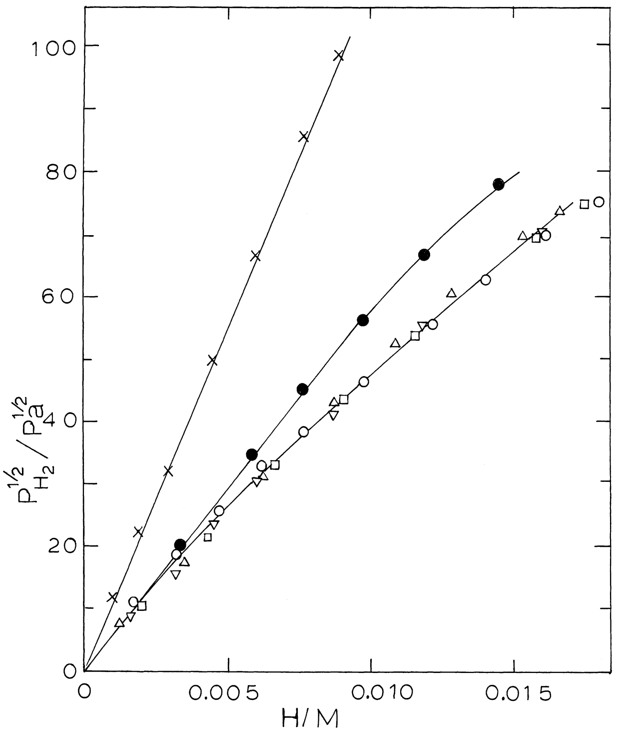

Fig. 1. Dilute phase solubilities (323 K) for Pd–Fe alloys. (○) Pd; (▽) $X_{Fe} = 0.003$; (△) $X_{Fe} = 0.01$; (□) $X_{Fe} = 0.018$; (●) $X_{Fe} = 0.037$; (×) $X_{Fe} = 0.074$.

which *do* extrapolate to the value for Pd–H as would be expected and, therefore, the behavior of the Pd–Fe alloys can be considered anomalous. The reason for these anomalous H_2 solubilities in Pd–Fe alloys at small X_{Fe} may be related to the lattice parameter dependence on X_{Fe}. Although there is some scatter, the lattice parameters appear to extrapolate at $X_{Fe} = 0$ to a parameter greater than that of pure Pd [2,3]. The anomalous hydrogen solubilities are consistent with this lattice parameter behavior because the H_2 solubilities are greater in "expanded" Pd alloys than in Pd [8].

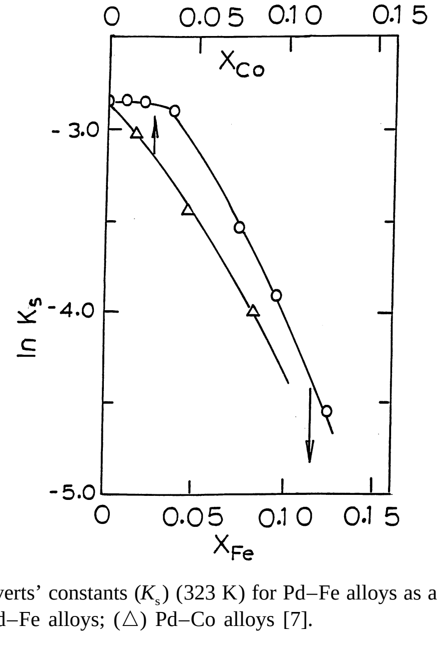

Fig. 2. Sieverts' constants (K_s) (323 K) for Pd–Fe alloys as a function of X_{Fe}. (○) Pd–Fe alloys; (△) Pd–Co alloys [7].

Relative partial molar thermodynamic properties were determined in the dilute phase for Pd–Fe alloys from H_2 solubility data as a function of temperature in the earlier investigation [1]. In this method the relative partial enthalpies are obtained at different r values from the slopes of plots of $R\ln p_{H_2}^{1/2} = ((\mu_H - \frac{1}{2}\mu_{H_2}{}^{\circ})/T)$ against $1/T$ [9]. As expected, the relative partial enthalpies of H_2 solution decrease in magnitude with increase of X_{Fe}. The relative partial entropy at infinite dilution, $\Delta S_H{}^{\circ}$, evaluated using the assumption that all of the interstices are available for occupation, decrease with X_{Fe} indicating that the presence of Fe excludes some adjacent octahedral interstices from occupation by H. This result is consistent with the Mössbauer results of Karger et al. [10] who concluded that there is a strong repulsive force between the Fe and any nearest neighbor H atoms in Pd–Fe alloys.

3.2. Complete hydrogen isotherms and plateau thermodynamic parameters

In the earlier study of the Pd–Fe–H system [1] thermodynamic data were not determined for the plateau regions, i.e., the two-phase region where the dilute and hydride phases co-exist. From the isotherm results obtained here the two phase region persists to a content between $X_{Fe} = 0.10$ and 0.12 at 303 K. This agrees quite well with the results of Carlow and Meads [2] who reported that the two phase region disappears above $X_{Fe} = 0.115$ at 298 K. Fig. 3 shows isotherms at 323 K where it can be seen that the two phase region no longer exists at about $X_{Fe} \geq 0.09$. The upper phase boundary is seen to decrease markedly with increase of X_{Fe}.

The only other (Pd+M+H) system, where M is an element in the Fe column of group VIII, which has been investigated is that where M=Ru [11]. For this system isotherms have only been measured at 373 K where the two phase region disappears at about $X_{Ru} = 0.10$. The phase diagram has the same shape as the diagram of the (Pd+Fe+H) system (Fig. 3) because the upper phase boundary also decreases markedly with X_{Ru}. Fe suppresses the extent of the two phase co-existence region more than Ru.

The thermodynamic properties corresponding to the plateau reaction:

$$\frac{1}{2}H_2(g,1\text{ bar}) + (1/(b-a))MH_a = (1/(b-a))MH_b \quad (1)$$

where a and b are the compositions of the co-existing dilute and hydride phase boundaries, have been determined from van't Hoff plots of the plateau pressures. Because of hysteresis, the van't Hoff plots give two sets of thermodynamic parameters which differ slightly in magnitude depending on the extent of hysteresis. The results are

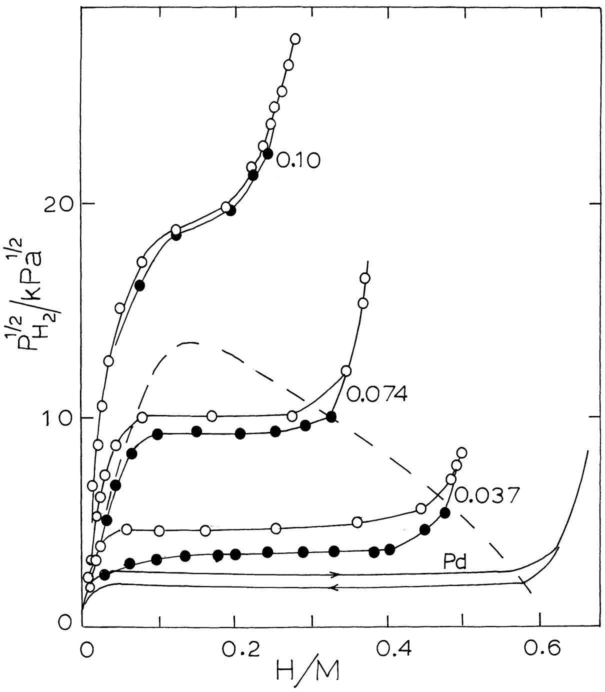

Fig. 3. Complete H_2 isotherms (323 K) for Pd–Fe alloys where the compositions are indicated on the isotherms by the value of X_{Fe}. The open symbols are for absorption and the filled ones for desorption.

shown in Table 1 where $|\Delta H_{plat}|$ decreases with X_{Fe} but the ΔS_{plat} values do not change very much. Results are also included for the $X_{Fe}=0.125$ alloy which does not form a plateau at 300 K but thermodynamic parameters are reported for $r=0.1$ which is close to the midpoint of the plateaux for the other Pd–Fe alloys.

Van Mal et al. [12] pointed out many years ago that for metal–hydrogen systems which form hydrides an appropriate value for ΔS_{plat} is -63 ± 12 J/K mol $\frac{1}{2}H_2$ for reaction (1). More recently a value of -54 ±2 J/K mol $\frac{1}{2}H_2$ was recommended as more suitable for AB_5–H systems [13] and a value of $\Delta S_{plat}=-46$ ±2 J/K mol $\frac{1}{2}H_2$ for Pd- and Pd-rich alloy–H systems [14]. The latter value falls outside of the predicted range given by van Mal et al. The difference in plateau entropies between Pd-rich alloys and AB_5-based alloys is of interest. It must be due partly to occupation of octahedral interstices in Pd-alloys and occupation of mainly tetrahedral ones for the AB_5 intermetallics. The H vibrational frequencies in tetrahedral interstices are greater than in octahedral interstices [9]. This means that H atoms in octahedral interstices have a greater vibrational entropy and consequently a less negative entropy change for H_2 absorption than for H in tetrahedral interstices.

Table 1
Thermodynamics parameters for hydride formation and decomposition in Pd–Fe alloys from this research (enthalpies are units of kJ/mol $\frac{1}{2}H_2$ and entropies in units of J/K mol $\frac{1}{2}H_2$)[a]

X_{Fe}	$\lvert\Delta H_{p-c-T}\rvert$	$\lvert\Delta S_{p-c-T}\rvert$	$\lvert\Delta H_{cal}\rvert$	$\lvert\Delta S_{cal}\rvert$	$\lvert\Delta H_{estim}\rvert$
0	18.5 (19.5)	46 (46)	19.1	46.3	19.1
0.037	15.0 (18.2)	49 (48)	16.5	43	17.3
0.074	14.0 (16.2)	43 (49)	15.0	44	15.0
0.10	13.3 (13.3)	46 (46)	13.5	43	13.3
0.125	–	–	12.0	46	–

[a] The values shown with and without parenthesis are for hydride formation (absorption) and decomposition (desorption), respectively, derived from the corresponding van't Hoff plots.

In view of the good approximation that $\Delta S_{plat}=-46$ ±2.0 J/K mol $\frac{1}{2}H_2$ for Pd-rich alloy–H systems, it should be possible to use this, and the experimental $\Delta G_{av.,plat}=\frac{1}{2}RT\ \ln(p_f\ p_d)^{1/2}$ values to estimate values of ΔH_{plat} where the av. subscript refers to the geometric average of p_f and p_d. If these estimations prove to be good, then it would have the great advantage of providing a method to obtain ΔH_{plat} values for previously unexamined Pd-alloys from plateau p_{H_2} data at a single temperature. Enthalpies estimated in this way are shown in the last column of Table 1 and the agreement with the experimental calorimetric values is generally good. It is reasonable to compare these estimates with the hysteresis-independent calorimetric or average enthalpies from the formation and decomposition van't Hoff plots because the estimated enthalpies should independent of hysteresis since $\Delta G_{av.,plat}$ and $\Delta S_{plat}=-46$ mol $\frac{1}{2}H_2$ are independent of hysteresis [15].

The values of hysteresis, $\frac{1}{2}RT\ \ln(p_f/p_d)$ where p_f and p_d are the hydride formation and decomposition plateau pressures, for the Pd–Fe alloys are about constant and equal to that for pure Pd–H up to $X_{Fe}=0.037$ and then hysteresis decreases with X_{Fe} to nearly zero at $X_{Fe}=0.10$ where the extent of the two-phase plateau region becomes very small (323 K).

Cycling Pd alloys through the hydride phase at ambient temperatures has been shown to decrease p_f and to increase p_d with the decrease of the former generally greater than the increase of the latter [16]. Thus cycling causes the two plateau pressures to approach each other and therefore to approach the equilibrium state more closely because the indications of irreversibility such as hysteresis and plateau sloping are reduced. The effect of cycling has been found to increase with atom fraction of solute, M, but the detailed changes depend on the nature of M and, for larger atom fractions of solute where the plateau extent becomes small, the effect of cycling diminishes [16]. For Pd–Fe alloys an appreciable number of hydriding/dehydriding cycles are required before the plateau pressures change significantly. For example, there is very little change for the $X_{Fe}=0.0375$ alloy after three cycles but, after seven cycles, hysteresis, $\frac{1}{2}RT\ \ln(p_f/p_d)$, has decreased from 840 to 400 J/mol $\frac{1}{2}H_2$.

3.3. Reaction calorimetric determination of enthalpies

Hydrogen reaction calorimetry was employed for the determination of the enthalpies and some typical results are

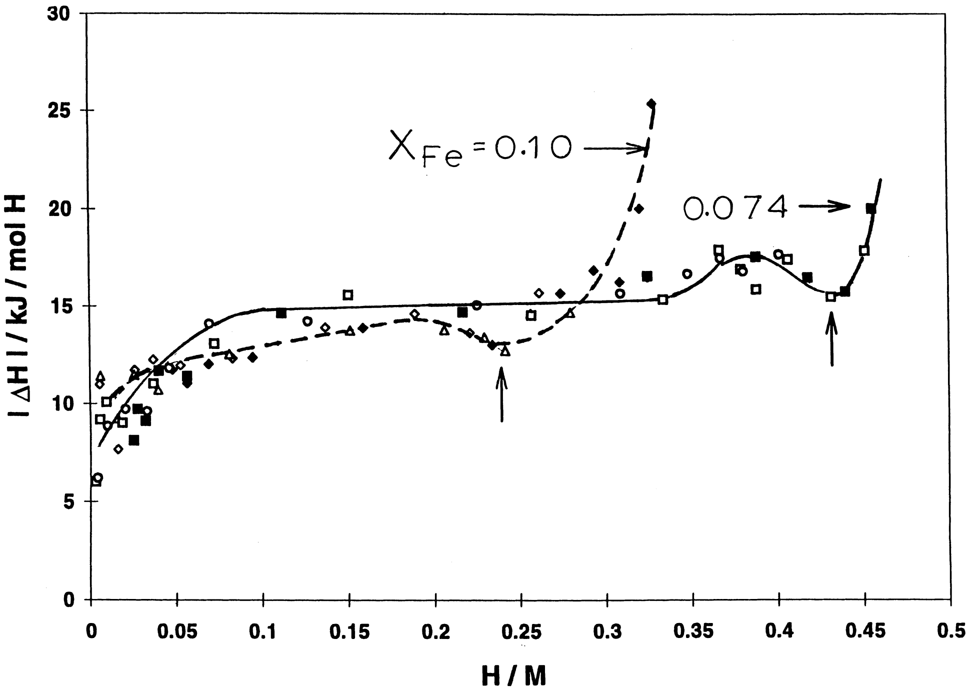

Fig. 4. Reaction calorimetric results for the $X_{Fe}=0.074$ and 0.10 alloys (300 K) where the compositions are indicated on the curves drawn through the data points. The vertical arrows indicate where there appears to be a minimum in the plots. (□), (○): $X_{Fe}=0.074$; (◇), (△): $X_{Fe}=0.10$. The open symbols are for absorption and the filled ones for desorption.

shown in Fig. 4 for the $X_{Fe}=0.074$ and 0.10 alloys (300 K). Results are given for measurements where heat is evolved (absorption of H_2) or absorbed (desorption of H_2) and there is no significant difference between the absorption or desorption $|\Delta H_{cal}|$ values. The $X_{Fe}=0.10$ alloy–H system should lie just within the miscibility gap at 300 K according to [2]. Calorimetric measurements were also carried out for other Pd–Fe alloys and the results for the plateau reactions are shown in Table 1.

Values of ΔS_{plat} can be determined from the calorimetrically measured enthalpies (Fig. 4) and the isotherms measured at a given temperature (Fig. 5) using

$$\Delta S_{cal}=\Delta H_{cal}/T-R\ln p_{H_2}^{1/2}, \tag{2}$$

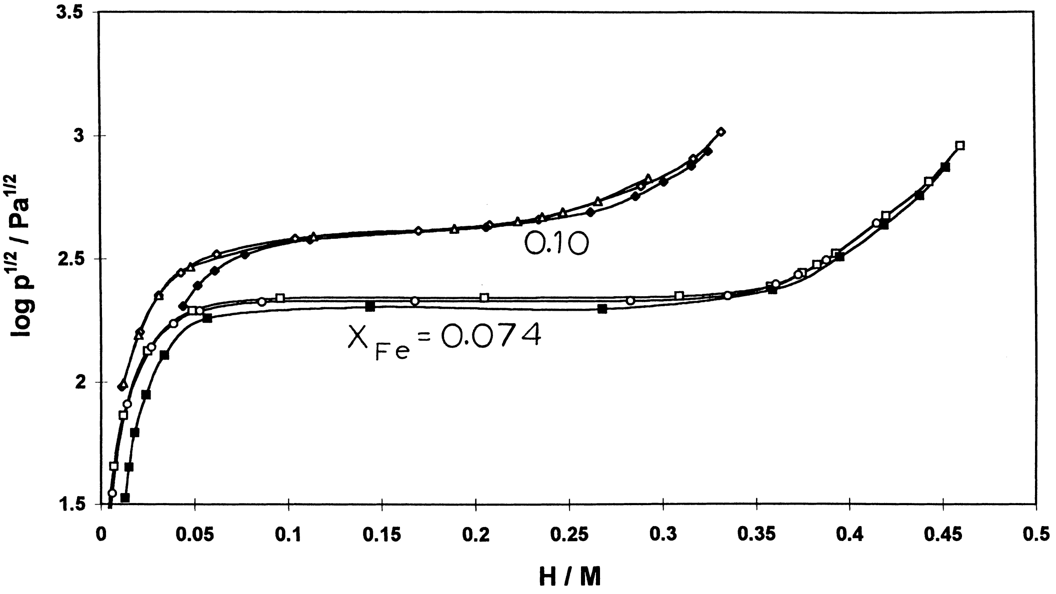

Fig. 5. Complete H_2 isotherms (300 K) corresponding to the calorimetric results shown in Fig. 4. (□), (○): $X_{Fe}=0.074$; (◇), (△): $X_{Fe}=0.10$. The open symbols are for absorption and the filled ones for desorption.

where p_{H_2} is taken as $(p_f \; p_d)^{1/2}$ for the plateau region. These values are shown in Table 1 as ΔS_{cal}.

It has been shown on thermodynamic grounds for metal–H systems that, when the upper phase boundary decreases with increasing temperature, there must be a step in the $|\Delta H| - r$ and $|\Delta S| - r$ relations at the phase boundary between the plateau and the adjacent single phase hydride regions [17]. The upper phase boundaries decrease with temperature for the Pd–Fe alloys (not shown here because of space limitations) and therefore steps in the thermodynamic parameters should appear at the phase boundaries. It should be pointed out, however, that well-defined discontinuities are not expected because finite increments of H must be added or removed during the calorimetric measurements and therefore in the H content region close to phase boundaries both the plateau and adjacent single phase enthalpies will contribute to the measured values causing predicted discontinuities to change into rather abrupt changes of slopes. This appears to be the case for the $X_{Fe} = 0.074$ alloy–H system where the discontinuity is indicated by the hump at about $r = 0.37$ which corresponds to the end of the plateau region (Fig. 5). For the $X_{Fe} = 0.10$ alloy the situation is not as clear because the two phase region is quite small due to the proximity of the compositions to the critical point.

For both the alloys shown (Fig. 4) the $|\Delta H_H|$ values appear to decrease after the maximum and then increase in the hydride phase region as r increases. Thus the $|\Delta H| - r$ relations for these Pd–Fe alloy–H systems resemble those for $Pd_{0.915}Co_{0.085}$–H [7] and $Pd_{0.90}Ni_{0.10}$–H [18]. The Pd–H system behaves differently because $|\Delta H|$ jumps to a higher value from its plateau value and then falls steadily [6]. Of course, for pure Pd–H and all the other Pd alloys, p_{H_2} must increase with H content, e.g., (Fig. 5), but the increase of p_{H_2} in the hydride phase region has different thermodynamic origins for Pd–H and the cited alloys because of the different trends in behavior of their partial thermodynamic parameters with r.

It has been shown from thermodynamic arguments that calorimetric plateau enthalpies should not be affected by hysteresis [15] and it has been shown that the average of the values derived from the formation and decomposition van't Hoff plots should be close to the calorimetric enthalpies [15]. The results shown in Table 1 tend to confirm this because the plateau enthalpies determined calorimetrically and the average of the enthalpies from the van't Hoff plots agree reasonably well (Table 1).

For metal–H systems ΔS_H can be represented in single phase regions by [9]

$$\Delta S_H = \Delta S_H{}^{\circ} - R \ln(r/(\beta - r)) + S_H^{\text{non-id.}}, \tag{3}$$

where $-R \ln(r/(\beta - r))$ is the partial ideal configurational entropy contribution and β is the fraction of occupiable octahedral interstices and $S_H^{\text{non-id.}}$ refers to any non-ideal, r-dependent contributions to the partial entropy.

The composition of the $X_{Fe} = 0.10$ alloy is close to the critical composition and, consequently, over most of its concentration range, p_{H_2} and the thermodynamic parameters change continuously with r at least up to $r \approx$ 0.13.

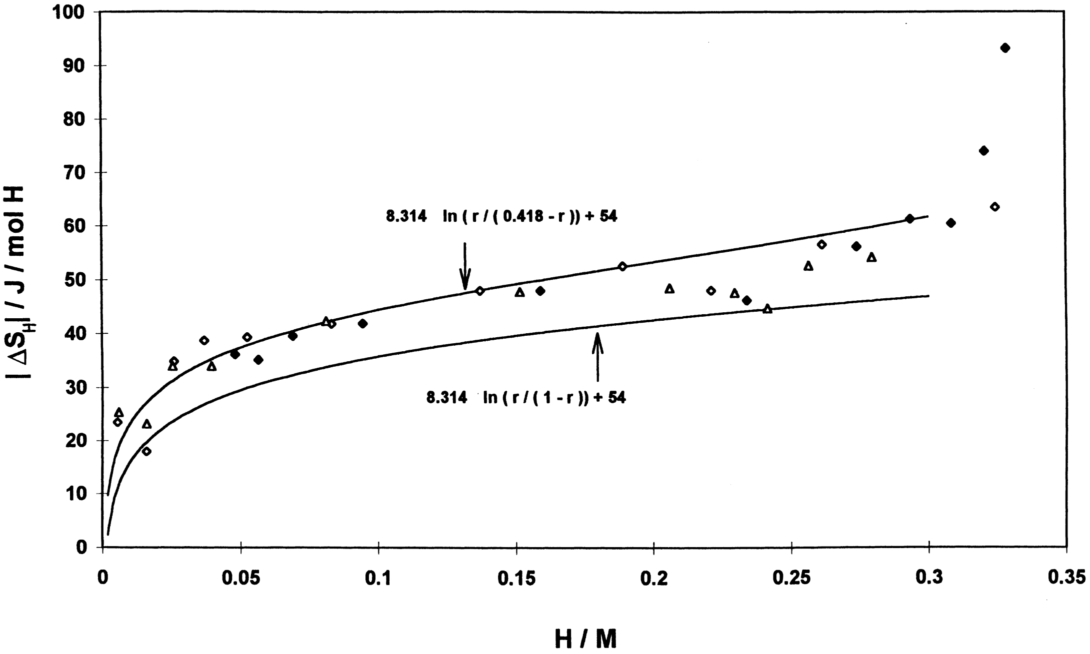

Fig. 6. Experimental ΔS_H values for the $X_{Fe} = 0.10$ alloy calculated from the p_{H_2} (300 K) and the calorimetric results shown in Fig. 4. The two labeled solid lines correspond to values calculated by the equations shown and discussed in the text. The open symbols are for absorption and the filled ones for desorption.

Fig. 6 shows experimental plots of ΔS_H compared with the calculated values of the first two terms in Eq. 3 for the $X_{Fe} = 0.10$ alloy where ΔS_H° is taken as -54 J/K mol $\frac{1}{2}H_2$ and two choices for β have been employed, 1 and 0.418. It can be seen that the agreement is better for the latter choice of β, at least in the low H content region, which is consistent with the findings of Karger et al. that H prefers to avoid the interstices with Fe nearest neighbors [10]. A non-ideal entropy contribution is found for the Pd–H [19,20] systems which is increasingly negative with r up to 0.24 and then decreases and becomes positive for $r > 0.50$. It seems from the experimental results (Fig. 6) that the non-ideal partial entropy must be positive for the $X_{Fe} = 0.10$ alloy for $r > 0.16$.

3.4. Conclusions

The dilute phase solubility for Pd–Fe alloys appears to be anomalous because the solubility data as $H \rightarrow 0$ do not extrapolate at $X_{Fe} = 0$ to the value for Pd–H. The plateau pressures of the H_2 isotherms increase with X_{Fe} which is consistent with their categorization as contracted alloys having smaller unit cells than Pd. The enthalpies for formation/decomposition of the hydride phase, the plateau reaction, decrease in magnitude with increase of X_{Fe} as found for both calorimetric and van't Hoff plot measurements. The corresponding entropies do not change very much, confirming that the average magnitude for Pd and its alloys is 46 ±2 J/K mol $\frac{1}{2}H_2$. It is demonstrated that a reasonable estimate for plateau enthalpies of Pd-rich alloy–H systems can be obtained from the characteristic magnitude for the entropy, 46 J/K mol $\frac{1}{2}H_2$, and the measured $\Delta G_{plat} = RT \ln p_{H_2}^{1/2}$.

Acknowledgements

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