JOURNAL OF SOLID STATE CHEMISTRY 120, 90–95 (1995)

The Solubility of Hydrogen and Deuterium in Crystalline Pd_9Si_2

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Received March 3, 1995; in revised form June 30, 1995; accepted July 5, 1995

Isotherms have been measured for $H(D)_2(g)$ solution in crystalline Pd_9Si_2 in the temperature range from 235 to 373 K. The solubilities are significant, e.g., at 1.0 MPa (298 K), (H/Pd) = 0.052 or $Pd_9Si_2H_{0.47}$, however, there is no indication of hydride phase formation even down to 235 K at 1.0 MPa. The thermodynamic values for hydrogen solutions at infinite dilution of hydrogen are $\Delta H^\circ_H = -11.9$ kJ/mole $\frac{1}{2}H_2$ and $\Delta S^\circ_H = -50$ J/K mole $\frac{1}{2}H_2$. The former is more negative than for Pd–H_2 and the latter is somewhat more positive; but generally the values are not that different from Pd–H_2. The isotope effect is similar to that found for Pd–$H(D)_2$. © 1995 Academic Press, Inc.

INTRODUCTION

After the first investigations by Spit *et al.* (1) of hydrogen absorption by Ni–Zr(Ti) amorphous alloys, Pd–Si alloys were the next amorphous alloys investigated (2–4). The interpretation of the results on the Pd–Si amorphous alloys illustrated the important idea that the interstices in amorphous materials present a spectrum of interstitial energies for hydrogen occupation (3). It was also noted experimentally that a hydride phase did not form. The latter was shown theoretically by Griessen (5) and others (6) to be a consequence of the site energy distribution and hydride formation should not occur when the energy spread of the interstices exceeds a certain minimum value. Of the amorphous Pd–Si alloys whose hydrogen solubilities have been studied, the composition $Pd_{82}Si_{18}(Pd_{9.1}Si_2)$ is closest to that of the crystalline Pd_9Si_2 alloy. The latest research with the $Pd_{9.1}Si_2$ amorphous alloy (7) cites the earlier references on hydrogen solution in amorphous Pd–Si alloys.

Few investigations of hydrogen absorption by the crystalline counterparts to the amorphous Pd–Si alloys have been carried out. The comparison of the results of hydrogen absorption by the amorphous and crystalline forms of the same alloy composition may offer some insights. Feenstra *et al.* (4) investigated hydrogen absorption by amorphous and crystalline Pd_4Si alloys. There is controversy, however, about the existence of the Pd_4Si phase and the latest assessment of the complete phase diagram for the Pd–Si system (8) does not include it. For this reason, the results of the investigation by Feenstra *et al.* on the crystalline material are ambiguous. Otherwise, there seems to be no investigations of hydrogen uptake by crystalline Pd–Si phases. Pd_9Si_2 is a well defined phase (8) which forms peritectically at a temperature of 1096 K. It has an orthorhombic structure and the space group is *Pnma* (9). The structure is characterized by augmented triangular prismatic coordination of the silicon atoms such as that which occurs in several metal-rich transition metal silicides, e.g., Co_2Si (10).

Andersson *et al.* (11) have recently shown from neutron diffraction that deuterium occupies the square pyramidal interstices in $Pd_9Si_2D_{0.22}$, i.e., those coordinated by five nearest neighbor Pd atoms. The full occupation of these interstices leads to the stoichiometry Pd_9Si_2D. These were found to be the only interstices occupied up to $n = 0.22$ where $n = D/(Pd_9Si_2)$. This unusual interstitial occupation by D has also been found in some Pd–P phases (12–14) although in these systems other interstices are occupied simultaneously. Such a coordination of interstitial hydrogen in ZrCo has also been suggested on the basis of the hydrogen inelastic neutron scattering spectra in ZrCo where the simultaneous occupation of tetrahedral and pyramidal sites was proposed (15). In Pd_9Si_2D the D atoms are greater than 0.35 nm apart (11) and therefore possible blocking of an interstice by D (or H) in an adjacent interstice would not be expected to be a factor; the interstices should be therefore occupied in a completely random way. In the β-phase of pure Pd by comparison, the D atoms can be as close as 0.284 nm. In contrast to the other systems where pyramidal sites are occupied (12–14), these are the only ones occupied over a large pressure range in Pd_9Si_2D

0022-4596/95 $12.00

and therefore the solubility data should be amenable to interpretation using a particularly simple model. The expected absence of blocking in Pd_9Si_2 suggests that the excess entropy should vanish as long as these are the only interstices occupied. It will be of interest to examine these predictions experimentally.

EXPERIMENTAL

Pd_9Si_2(c) was prepared by arc-melting stoichiometric amounts of palladium sponge (Johnson and Matthey Co., 3N5) and silicon (5N). The melted sample was heat-treated in an evacuated silica tube at 1055 K for 3 months. It was single phase material judging from the X-ray diffraction pattern. Hydrogen (deuterium) solubilities were measured from the pressure changes in known volumes. The pressures were measured with a series of MKS Baratron gauges.

RESULTS AND DISCUSSION

Hydrogen Solubilities

Pd_9Si_2 was found to be quite stable and did not exhibit any changes of hydrogen solubility behavior as a result of cycles of hydrogen absorption and desorption. The kinetics were quite favorable enabling equilibrium data to be obtained down to low temperatures, e.g., 235 K. This means that the diffusion constant for hydrogen is quite fast, i.e., comparable to pure palladium. This is surprising because the diffusion constant generally falls when palladium is alloyed with substantial amounts of solutes (16) and because hydrogen tends to avoid the neighborhood of the Si atoms (17).

It is of interest to compare the solubilities of hydrogen in Pd_9Si_2(c) and in the amorphous $Pd_{9.1}Si_2$ ($Pd_{82}Si_{18}$) alloy. At 0.1 MPa and 298 K the latter is r = (H/Pd) = 0.018 (7) and in the present work, under the same conditions, it was found that the solubility in the crystalline compound is r = 0.0256 or a ratio of 1.42 for the relative hydrogen solubilities in the amorphous and crystalline forms. Under somewhat different conditions, 333 K and 0.4 MPa, Feenstra *et al.* (4) found a ratio of 1.49. Thus there is a greater solubility in the crystalline form, however, the solubilities in the two different forms of the alloys are surprisingly similar in view of the different structures of the crystalline and amorphous phases. Results from measurements of neutron inelastic scattering has suggested that both tetrahedral and octahedral (distorted) sites are occupied by H in amorphous $Pd_{11.3}Si_2$ judging from the vibrational spectra measured by neutrons (18).

Typical isotherms for H_2 dissolved in Pd_9Si_2(c) are shown in Fig. 1, where, similarly to the results found for hydrogen solubility in the amorphous and crystalline Pd–Si alloys studied by Feenstra *et al.* (4), there are strong positive

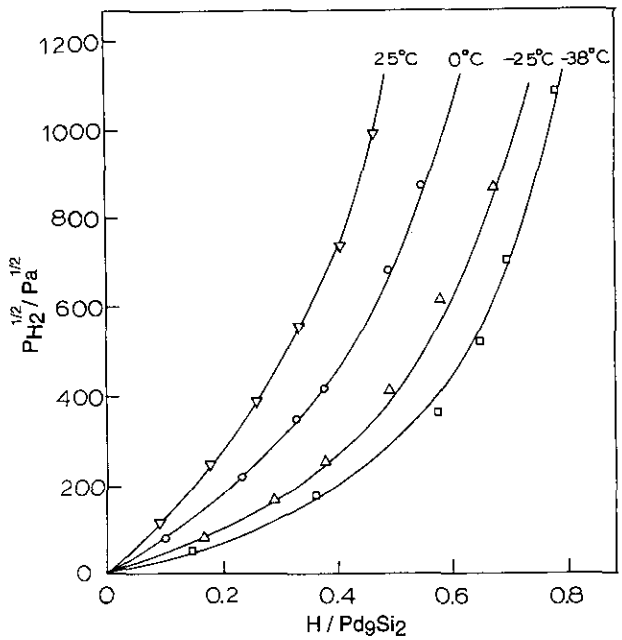

FIG. 1. Hydrogen absorption isotherms for Pd_9Si_2(c) plotted as $p_{H_2}^{1/2}$ as a function of n = H/(Pd_9Si_2). ▽, 298 K; ○, 273 K; △, 248 K; □, 235 K. The solid curves are calculated from Eq. [1] and the data in Table 1.

deviations from Sieverts' law as $(H/M) = r$ increases from 0. Because of the contrast of these positive deviations from Sieverts' law with the negative deviations found in pure Pd, which is the major component of the alloy, Feenstra *et al.* have noted this to be the most striking feature of these hydrogen solubilities. In Pd–H the negative deviations lead to hydride formation below the critical temperature (19). Feenstra *et al.* suggest that this indicates a repulsive interaction between the H atoms in Pd_9Si_2. It is argued below, however, that this conclusion does not follow from such positive deviations. In any case, there is no sign of a two phase plateau region even to the highest contents and lowest temperatures measured.

According to the most recent assessment of the Pd–Si phase diagram (8), amorphous Pd_4Si should decompose into Pd_3Si(c) and Pd_9Si_2(c) upon heating at 577 K which was the condition employed by Feenstra *et al.* to obtain the crystalline compound reported by them to be Pd_4Si(c). Pd_3Si(c) does not absorb significant amounts of hydrogen (11) and therefore the solubility which they determined can be attributed entirely to the fraction of Pd_9Si_2(c) in their crystallized material. On this basis, the solubility in their crystalline compound, when corrected for the fraction of Pd_9Si_2(c), should agree with the present data. Excellent agreement is obtained if the composition of their material were to have been $Pd_{79.5}Si_{20.5}$ instead of $Pd_{80}Si_{20}$, which is probably within experimental error of their stoichiometry. In Fig. 2 their data, which has been corrected for the ex-

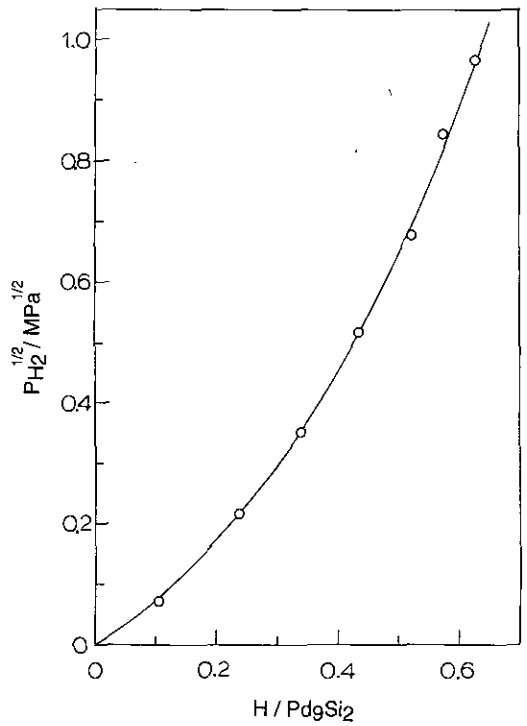

FIG. 2. Plot of $p_{H_2}^{1/2}$ against n = (H/Pd_9Si_2) at 333 K. The solid line is from the present results and the data shown by O are from the data of Feenstra *et al.* (4) after correction of their data for the fraction of Pd_9Si_2(c) in their sample and assuming that Pd_3Si does not absorb any H_2 under these conditions.

pected fraction of Pd_9Si_2(c), are shown at 273 K compared with the present results. The very similar shapes of the $p_{H_2} - r$ relations suggest that in each case the same phase is absorbing the hydrogen.

The crystallized amorphous compound $Pd_{80}Si_{20}$, whose hydrogen solubility was studied by Feenstra *et al.*, must consist of Pd_3Si(c) and Pd_9Si_2(c) as noted above. The positive deviations from Sieverts' law were attributed to the dominant role of the electronic term due to band filling as compared to the elastic interaction contribution (4). Based on the present results, another interpretation seems to be more likely in view of the structural results from neutron diffraction (11); namely, it seems clear that the positive deviations are almost entirely due to configuration effects arising from the availability of interstices for H occupation. Since $Pd_{80}Si_{20}$(a) should crystallize according to the phase diagram mainly into Pd_9Si_2(c), the deviations from Sieverts' law found by Feenstra *et al.* must also be due to the configurational term. The value of $\Delta S_H^\circ = -71$ J/K mole H reported by Feenstra *et al.* becomes −48.2 J/K mole H when allowance is made for the number of interstices per formula unit; this is in closer agreement with the value of −50 J/K mole H found here evaluated for one interstitial site per formula unit Pd_9Si_2(c). The value of −71 J/K mole H is more characteristic of tetrahedral occupation of interstices which is not the case for Pd_9Si_2(c). The isotope effect is also consistent with the lower entropy magnitude, i.e., both depend on the vibrational frequency of the H. Feenstra *et al.* did report from their experimental data that the values of ΔH_H increased as r increased from 0 to 0.02 giving a slope of 50 kJ/mole H which was consistent with the values obtained from their plots of $RT \ln (p_{H_2}^{1/2} (1 - r/r)$ against r. It seems, however, that the total change in ΔH_H of less than 1 kJ/mole H is not sufficiently accurate to reliably establish the dependence.

Thermodynamic Parameters at Infinite Dilution

The solution of hydrogen in metals can be described by the statistical mechanical equation

$$RT \ln p_{H_2}^{1/2} = \Delta H_H^\circ - T\Delta S_H^\circ + RT \ln (r/(\beta - r)) + \mu_H^E(r). \quad [1]$$

The standard superscripts indicate values at infinite dilution of H without the partial ideal configurational term, i.e., the third term on the right-hand-side of the equality sign, β is the number of interstices available for H occupation per metal atom, and the last term refers to the nonideal behavior. It is convenient to employ two different definitions of concentration for Pd_9Si_2, r = H/Pd and n = H/(Pd_9Si_2), where $n = 9r$. Equation [1] can be rearranged and expressed in terms of n as

$$RT \ln \left(\frac{(1 - n)p_{H_2}^{1/2}}{n} \right) = \Delta\mu_H^\circ + \mu_H^E(n). \quad [2]$$

When the left-hand-side of Eq. [2] is plotted against n at a given temperature, the values of $\Delta\mu_H^\circ$ are obtained from the intercepts at $n = 0$ (19, 20).

Thermodynamic parameters were determined for the Pd_9Si_2–H_2 system from isotherms measured between 235 to 383 K; some of these data are shown in Fig. 1. The parameters were determined using Eq. [2] as shown in Fig. 3. The plots are essentially horizontal indicating that μ_H^E is nearly zero. A plot of $\Delta\mu_H^\circ/T$ as a function of $1/T$ give ΔH_H° and ΔS_H° as the slope and intercept, respectively. The results are shown in Table 1 in comparison to values for Pd–H(D)$_2$. It should be reiterated that ΔS_H° has been determined from the temperature dependence of $\Delta\mu_H^\circ$ using Eq. [2] which utilizes the structural information from neutron diffraction (11) that there is only one interstice available for hydrogen occupation per formula unit, Pd_9Si_2(c). The value of ΔH_H° in Table 1 is slightly more exothermic than for Pd–H_2(D_2) (21) and the ΔS_H° value is slightly smaller in magnitude than that for Pd.

Figure 4 shows the solubilities of hydrogen in Pd_9Si_2(c) and in Pd as $r \to 0$, where both have been plotted as a

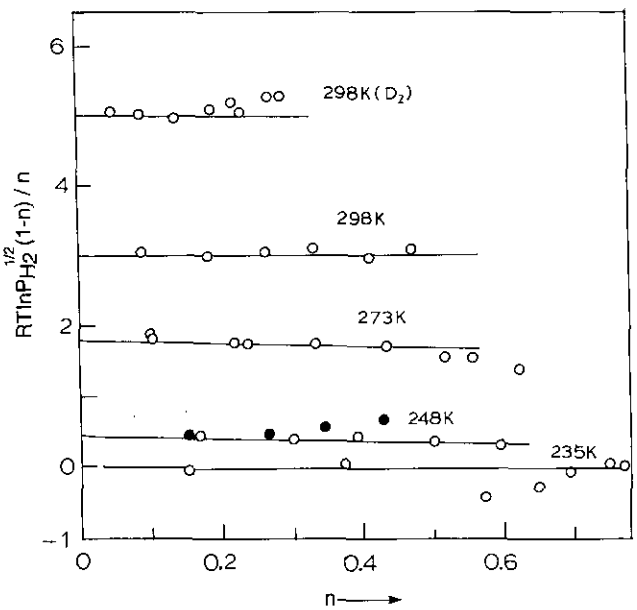

FIG. 3. Plots of $RT \ln p_{H_2}^{1/2} (1 - n)/n$ against n.

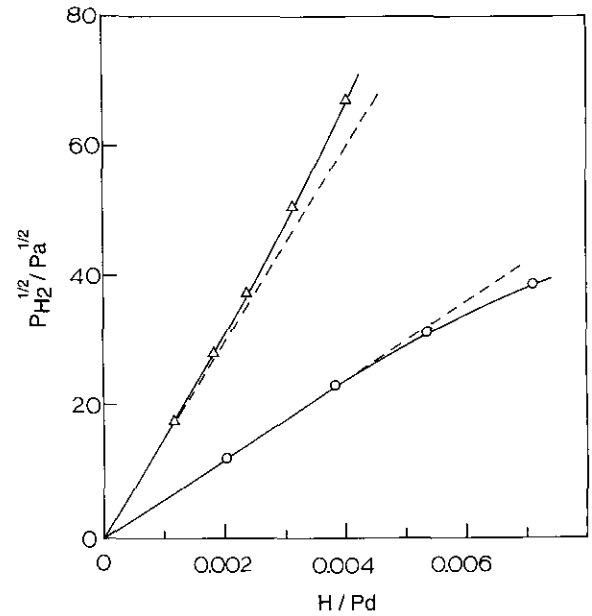

FIG. 4. Plot of hydrogen solubility in Pd and Pd_9Si_2(c) (333 K) as a function of r. △, Pd_9Si_2(c); ○, Pd. The dashed straight lines have been drawn to the origin and through the low hydrogen content data near the origin.

function of r. The slope of the former data is greater than for the latter, but, according to the relative enthalpies and entropies at infinite dilution (Table 1), the hydrogen solubility in Pd_9Si_2 should be greater than in Pd. The reason for this apparent anomaly is due to the fact that there is only (1/9) interstice available per Pd atom in Pd_9Si_2(c). This has been allowed for in the determination of ΔS_H° in Table 1 and if it were to be assumed that $\beta = 1$ in Eq. [1], then $\Delta S_H^\circ = 68.7$ J/K mole $\frac{1}{2}H_2$ which would reflect the actual difference in initial solubilities; i.e., it would cause the solubility in Pd_9Si_2(c) to be lower than for Pd.

It can be seen in Fig. 1 that there is no indication of a plateau region even at the lowest temperature measured, 235 K. The deviations from Sieverts' law are positive where Sieverts' law is

$$r = K_s' p_{H_2}^{1/2}. \qquad [3]$$

TABLE 1

A Summary of Thermodynamic Parameters for Hydrogen and Deuterium Solution in Pd_9Si_2 (c) and Pd at Infinite Dilution

Alloy	ΔH_H°	ΔS_H°	ΔH_D°	ΔS_D°
Pd_9Si_2	−11.9	−50.0	−9.5	−48.7
Pd	−10.2	−54.5	−8.6	−56.5

Note. The units of ΔH and ΔS are kJ/mole $\frac{1}{2}H_2$ and J/K mole $\frac{1}{2}H_2$ and the data for Pd–H(D) are from reference (20).

Sieverts' law is an experimental relation which applies as $r = H/M \to 0$. This equation can be derived from a simple consideration of thermodynamic equilibrium between H_2(g) and the dissociated H solute atoms. On the other hand, it is insightful to obtain it from Eq. [1], i.e., as $r \to 0$,

$$r = \left(\exp - \left(\frac{\Delta H_H^\circ - T\Delta S_H^\circ}{RT}\right)\right) \times \beta \times p_{H_2}^{1/2}. \qquad [4]$$

Often it is assumed that $\beta = 1$ and Sieverts' constant, K_s', then implicitly includes β as in Eq. [3]. In order, however, to obtain from the temperature dependence of the Sieverts' constant a meaningful value of ΔS_H°, i.e., a value which can be meaningfully compared for different metal–hydrogen systems, it seems best to include the β term explicitly as in

$$r = K_s \times \beta \times p_{H_2}^{1/2}. \qquad [5]$$

In pure metals, alloys, and intermetallic compounds there are generally ≥0.5 interstices available per metal atom and therefore it is a good approximation to replace $(\beta - r)$ by β as $r \to 0$ in the partial configurational chemical potential term, i.e., the second to last term in Eq. [1] becomes $RT \ln (r/\beta)$, for small values of r where Sieverts' law holds. It is therefore generally valid to equate obedience to

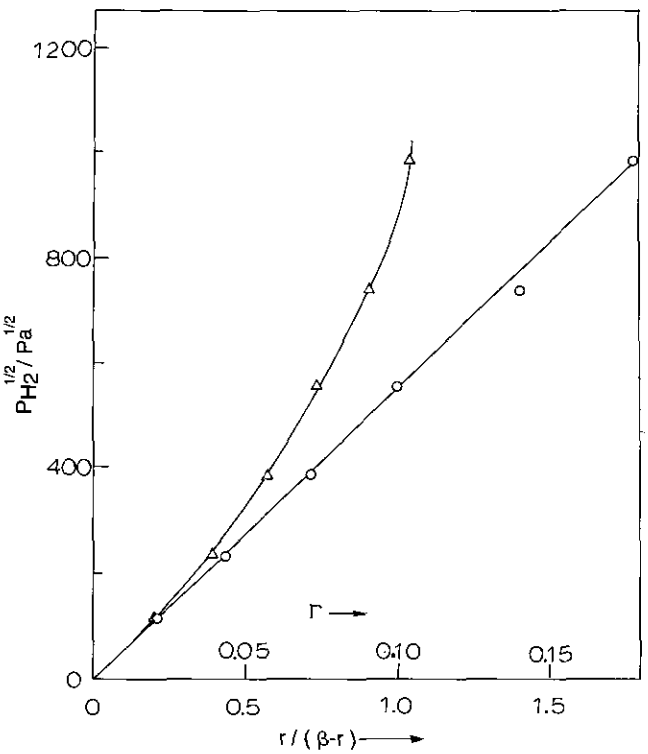

FIG. 5. Hydrogen solubility in Pd_9Si_2(c) (298 K) plotted as a function of r, △ (upper legend on the abscissa), and as a function of $r/(\beta - r)$, ○ (lower legend).

Sieverts' law with ideal behavior. For example, in Pd–H, deviations from Sieverts' law are caused by H–H attractive interactions before the term $(1 - r)$ in the denominator of the configurational term becomes significant. In the case of Pd_9Si_2(c), however, ideal behavior should not be equated with Sieverts' law because for each Pd atom there is only (1/9) of an interstice available and therefore the $(\beta - r)$ term cannot be considered to be constant even for quite small r values. This is illustrated by Fig. 5 where data for Pd_9Si_2–H at 298 K have been plotted via Eqs. [3] and

$$\frac{r}{\beta - r} = \frac{n}{1 - n} = K_s \times p_{H_2}^{1/2}. \qquad [6]$$

It can be seen that the plot via Eq. [6] is reasonably linear whereas the usual Sieverts' plot is not.

Description of H_2 Solubility at Larger H(D) Contents

In Fig. 1 the continuous curves show calculated results using Eq. [1] with $\mu_H^E = 0$ and the values of $\Delta\mu_H^\circ = \Delta H_H^\circ - T\Delta S_H^\circ$ shown in Table 1. It can be seen that there is reasonably good agreement over the whole range of n values, i.e., to an occupation of about 80% of the available interstitial sublattice (Fig. 1). By contrast, in Pd–H the excess, or nonideal, hydrogen chemical potential is appreciable even at relatively low H contents (22, 23) where both the partial enthalpy and entropy contribute to the excess chemical potential and it has been argued that the latter is mainly comprised of nonideal configurational entropy (23). It appears that the excess chemical potential of hydrogen is nearly zero to $r = 0.085$ for Pd_9Si_2 where it reaches a value of -4.6 kJ mole $\frac{1}{2}H_2$ for Pd–H (23). It is surprising that there is no detectable H–H attractive interaction in the Pd_9Si_2–H system because a long range interaction is expected due to the volume expansion of the lattice due to H in a sample of finite volume (24). If there were an H–H attractive interaction similar to that found in pure metals (25), the effect would have been experimentally detectable.

The behavior of the Pd_9Si_2–H system indicates that it is an ideal system with regards to the thermodynamics of hydrogen solution because the excess chemical potential is nil over the concentration range examined, i.e., up to 80% occupation of the interstices which are known to be occupied, and deviations from Sieverts' law simply arise from the denominator of the ideal configurational term. The authors are unaware of any other metal–hydrogen system which behaves in a similarly ideal manner.

Hydrogen vibrational frequencies were measured by inelastic neutron scattering for amorphous $Pd_{85}Si_{0.15}H_n$, $0.13 \leq n \leq 8.23$ (18); from these measured frequency values it was suggested that two different types of interstices were simultaneous occupiedly. On the basis of agreement with model calculations the Pd_6 octahedral and the Pd_3Si tetrahedral interstices were suggested to be occupied. The latter seems to be unlikely, however, in view of the general tendency for H to avoid interstices in the vicinity of p-elements as shown by Rundqvist *et al.* (17). In crystalline $Pd_9Si_2D_n$ only one type of site appears to be occupied up to $n = 0.22$ (11) and this is neither the tetrahedral nor octahedral site as suggested for the amorphous material.

$Pd_{82}Si_{18}(Pd_{9.1}Si_2)$ is the amorphous compound whose hydrogen solubility characteristics have been studied which is closest in composition to Pd_9Si_2. Szökefalvi-Nagy *et al.* (7) have measured isotherms for the former and fitted their data using an average site energy of -12.2 kJ/mole H with a Gaussian spread of energies of 13.9 kJ/mole H. The average site energy is similar to the value found here for crystalline Pd_9Si_2. In the amorphous material at 0.1 MPa (298 K) they found $r = 0.018$ (7) and for comparable conditions it is 0.0256 for Pd_9Si_2(c). The difference in these values is not very large. In view of the similarity in the hydrogen solubility behavior in the amorphous and crystalline forms of $Pd_{9.1}Si_2$(a)(4) and Pd_9Si_2(c), it seems likely that interstices with chemical environments similar to that in Pd_9Si_2(c) might be also occupied in the amorphous alloy.

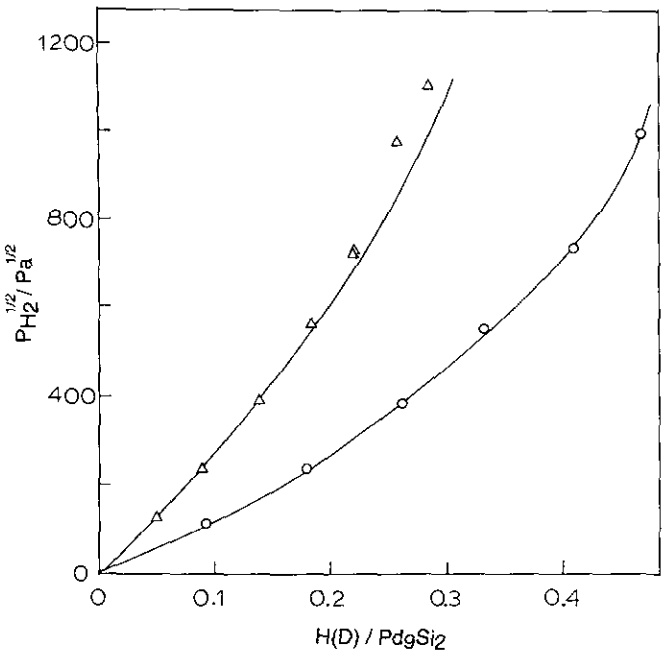

FIG. 6. Comparison of hydrogen and deuterium solubilities in Pd_9Si_2(c) at 298 K plotted as a function of n. ○, hydrogen; △, deuterium. The curves have been calculated from Eq. [1] employing data for hydrogen and deuterium given in Table 1.

Isotope Effect

Isotherms for Pd_9Si_2–D_2 were also measured and a typical isotherm is shown for 298 K in comparison with that for H_2 (Fig. 6). The isotope effect $\frac{1}{2}RT \ln (p_{D_2}/p_{H_2})$ is 2000 J/mole $\frac{1}{2}H(D)_2$ at 298 K. This is close to the value found for pure Pd–$H(D)_2$ (26), which is surprising in view of the fact that different kinds of interstices are occupied in Pd and Pd_9Si_2, i.e., octahedral and square pyramidal. The enthalpy values for deuterium are smaller in magnitude than for hydrogen by 1.8 kJ/mole $\frac{1}{2}H(D)_2$ compared to about 1.6 ± 0.2 kJ/mole $\frac{1}{2}H(D)_2$ for pure Pd (26) (Table 1).

CONCLUSIONS

The solubility of H_2 and D_2 in Pd_9Si_2(c) have been measured to quite low temperatures, 235 K. No evidence of a hydride phase has been found and thus the lack of a hydride phase in the amorphous alloys of similar compositions is not surprising. The spread in the site energies in the latter has been cited as the reason for this (27) but since it is also absent in the crystalline compound, the argument about site energies appears irrelevant for this amorphous/crystalline alloy. The solution of H_2 (D_2) in Pd_9Si_2(c) appears to be ideal over the entire range studied because the behavior can be described by Eq. [1] with $\mu_H^E = 0$ and $\beta = 1/9$. This makes Pd_9Si_2(c) a uniquely simple metal–hydrogen system from the statistical mechanical viewpoint. It is noteworthy that the energetics of hydrogen solubility in Pd–Si alloys appear to be largely independent of whether the alloy is in the amorphous or crystalline form.

ACKNOWLEDGMENT

T.B.F. acknowledges an NSF International Grant between the United States and Sweden which helped support this research.

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