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Absorption of hydrogen isotopes by Pd–Pt alloys

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Abstract

In the search for more profitable working materials for the recently developed gas chromatographic hydrogen isotope separation operated around room temperature without any replacement gas, thermodynamic properties of Pd–Pt alloys for hydrogen absorption and hydride formation were studied in the composition range 0–10 at.% Pt, the temperature range 273–493 K, and with a H/M from 2×10^{-4} to 0.65. The heat of absorption at infinite dilution and hydride formation were determined for H_2 and D_2. The results showed that both the heat of absorption and hydride formation decreased with increasing Pt content in the alloy and the isotope effect defined by the ratio of equilibrium pressures did not change much with alloy composition. It is implied that any alloy used in the present study could be selected as a working material depending on the required operation conditions without significant change in the separation efficiency. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Pd–Pt alloy; Hydrogen; Isotope; Absorption; Separation

1. Introduction

A variety of devices has been developed for the separation of hydrogen isotopes in fuel processing and waste handling for thermonuclear fusion reactors [1]. Among them, the liquid hydrogen distillation has been considered as the most promising method for fuel processing because of its high separation efficiency and large capacity. The gas chromatography is also promising for isotope separation because of its simple operation principle and construction, high separation efficiency and so on, and has been used in large-scale tritium-handling systems. Conventional gas chromatography is based on the isotope effect on physical adsorption of hydrogen isotopes by inert materials such as molecular sieves near 78 K. Although it has demonstrated excellent properties for separation, low-temperature chromatography requires a large amount of liquid nitrogen as a coolant. The other type is displacement chromatography where Pd is used as the working material for its large isotope effects on hydrogen absorption and hydride formation around room temperature [2]. It needs, however, rather complicated procedures and a fairly large amount of hydrogen as a replacement gas. In addition, it has a relatively large tritium inventory in the column [3,4].

A new gas chromatography technique developed recently can separate hydrogen isotopes near room temperature without any replacement gas using Pd–8% Pt as a working material [5–9]. More profitable working materials can be found in the Pd–Pt alloy system. From this viewpoint, the authors have studied the thermodynamic and kinetic features of hydrogen isotope absorption for Pd–Pt alloys to analyze the chromatographic separation. This paper describes the thermodynamic properties of the alloys for absorption and/or desorption of hydrogen and deuterium.

2. Experimental

Palladium and platinum plates were purchased from Nilaco. Their purities were guaranteed to be above 99.9%. Pd–Pt alloys were prepared from the raw materials by argon arc melting. Their filings below 100 mesh were used as samples. Gases used were purchased from Nihon Sanso with purities above 99.9999 and 99.7% for H_2 and D_2, respectively.

A high-vacuum system, denoted as System I, was used for absorption in a region where the equilibrium pressure was in the range 10^2–8×10^4 Pa. The block diagram is shown in Fig. 1. It consisted of a sample tube, standard volumeters, high-precision pressure gauges, gas reservoirs and vacuum pumps. Its residual pressure was routinely below 10^{-6} Pa. It was used for absorption measurements in the α-phase region. Another system was used to measure the isotherm where the equilibrium pressure was

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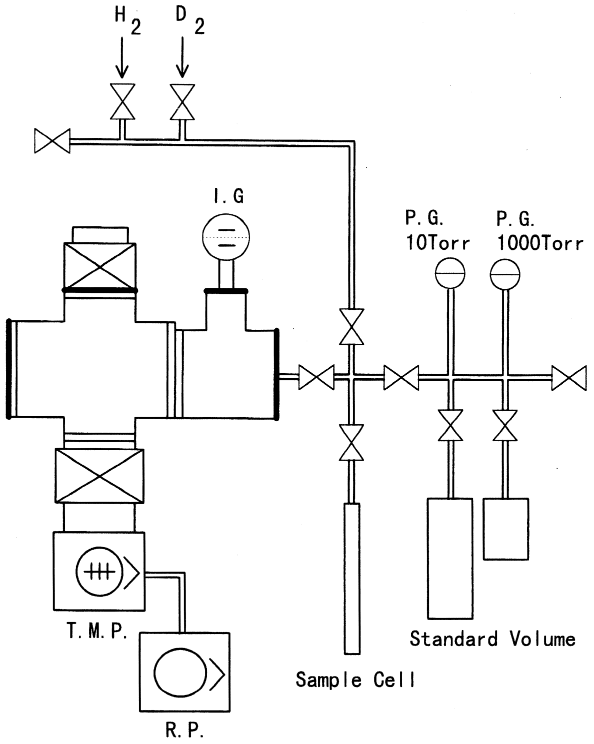

Fig. 1. Block diagram of System I for measuring absorption isotherms from 10^2 to 8×10^4 Pa.

in the range 1.0×10^3–5.1×10^6 Pa. This is denoted as System II. It consisted of a sample tube, a standard volume, pressure gauges, gas reservoirs and a vacuum pump. This device was used for the measurements of absorption and desorption isotherms in the ($\alpha+\beta$) region. Its construction was essentially the same as System I, except for the pressure gauges and the system volume.

Prior to absorption measurements, the sample powder was measured using X-ray diffractometry and ICPS (Radio-Frequency Inductively Coupled Plasma–Atomic Emission Spectroscopy) to examine the crystallinity and chemical composition, respectively. One and a half grams of alloy powder of 100–200 mesh was weighed out to set in the sample cell. For measurements in the α-phase absorption, System I was evacuated first below 10^{-6} Pa and then the sample was outgassed at 1073 K for 1 h as the activation treatment. As for measurements in the two-phase region, the same amount of sample was set in the sample tube and the system was evaluated below 10^{-5} Pa. Subsequently, the sample was degassed at 523 K for 2 h and activated by repeating hydrogen absorption and desorption cycles at given temperatures and then the system was evacuated. After the activation, the sample was cooled down and kept at a given temperature with an electric furnace or a water bath. The precision of the temperature control was within ±0.5 or ±0.1 K, respectively. The conventional constant volume method was used to obtain the P–C–T curves of the samples. To obtain a new isotherm, the sample was again degassed by heating at 250°C for 2 h.

3. Results and discussion

The X-ray diffraction analysis showed that the samples prepared had good crystallinity and gave the lattice constants as 3.889, 3.892 and 3.893 Å for 4, 8 and 10 at.% Pt alloys, respectively; these are in good agreement with the literature values. According to the ICPS analysis, their chemical compositions were 3.88, 8.05 and 9.83 at.%, respectively; however, they will be denoted as 4, 8 and 10 at.% Pt alloys for simplicity.

Fig. 2 shows the desorption isotherms of H_2 for Pd–4 at.% Pt in the temperature range 333–433 K. The isotherms showed a steep rise of equilibrium pressure for the α-phase absorption, then reached the plateau region of the $\alpha+\beta$ phase and finally rose again sharply. α-phase isotherms for this sample are shown in Fig. 3. The plot of $\sqrt{P}$ as a function of hydrogen concentration shows that Sievert's law holds in the very low concentration region up to about $x=0.005$, especially at low temperatures, suggesting that mutual interaction of dissolved hydrogen atoms plays a role in determining the solubility at higher concentration in the α phase.

It was observed that the equilibrium pressure of D_2 at a given temperature and concentration is always higher than that of H_2 in the whole H/M range measured in this study. Those features are also true for other alloys.

3.1. Absorption in the α-phase region

The absorption in the α-phase region was examined following Lässer and Powell [10] to obtain the equilibrium constant and to analyze its temperature dependence. The equilibrium constant for absorption of hydrogen or deuterium at the infinite dilution was determined from the plots using the following:

$$\ln\left[P\left(\frac{N-x}{x}\right)^2\right] = 2\ln K^\infty + \frac{2}{RT}\Delta\mu x \tag{1}$$

where P is the equilibrium pressure in atm. units, N is the number of interstitial sites per metal atom which is assumed to be unity, x is the hydrogen concentration (hydrogen-to-metal ratio), K^∞ is the equilibrium constant at infinite dilution, R is the gas constant, T is the temperature, and $\Delta\mu$ is the excess chemical potential. An example of such a plot according to Eq. (1) is shown in Fig. 4 for the 4 at.% Pt alloy. The plots resulted in fairly good straight lines for different temperatures. At each temperature, the slope is negative, which indicates that there is an attractive interaction between dissolved hydrogen atoms. This is also true for deuterium as well as other alloys.

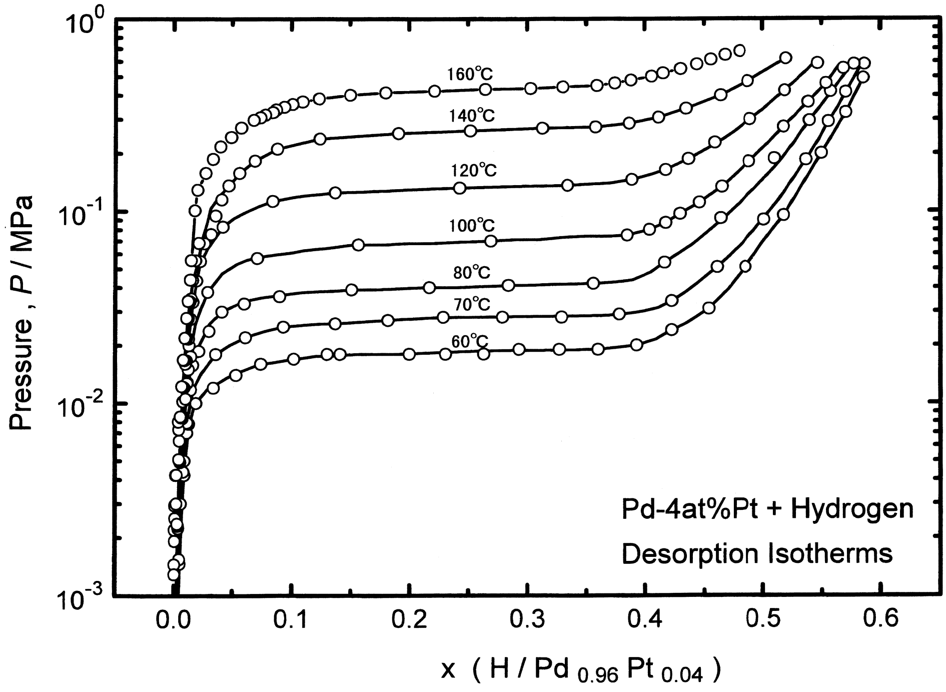

Fig. 2. Absorption–desorption isotherms of H_2 for Pd–4 at.% Pt. The part corresponding to the α phase shows the absorption isotherms measured using System I, and the one corresponding to the two-phase region shows the desorption isotherms obtained using System II.

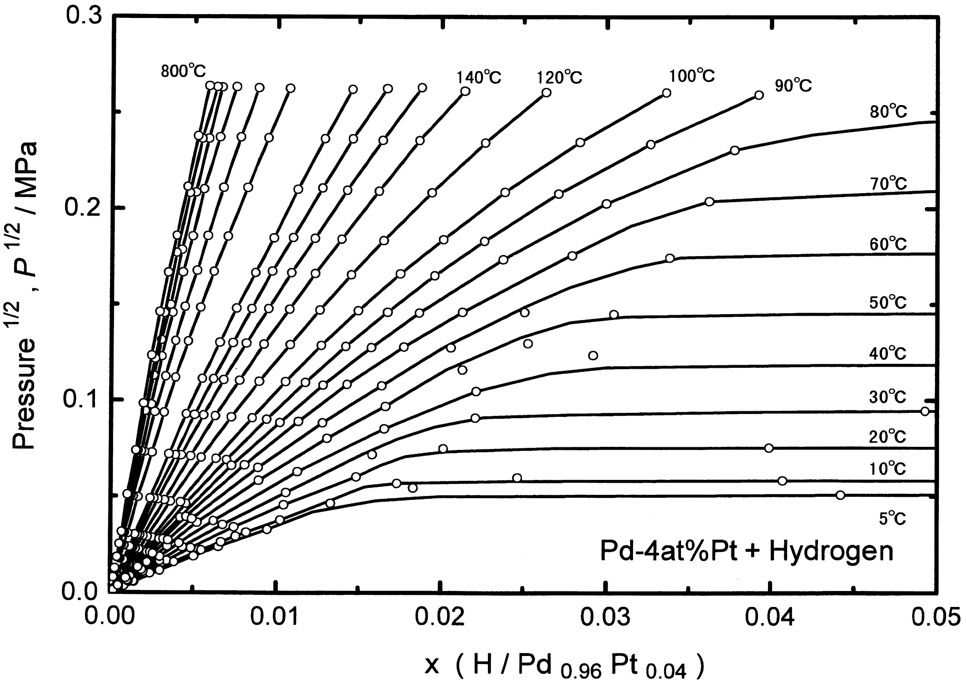

Fig. 3. Absorption isotherms of H_2 in the α-phase region for Pd–4 at.% Pt.

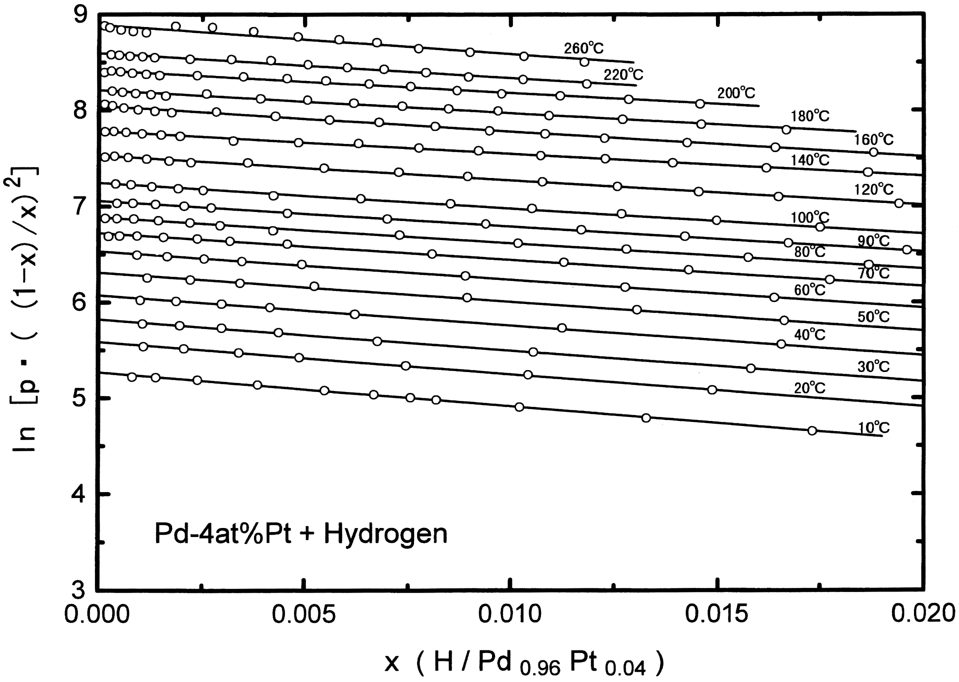

Fig. 4. Plot of $\ln[P((1-x)/x)^2]$ vs. H concentration for Pd–4 at.% Pt.

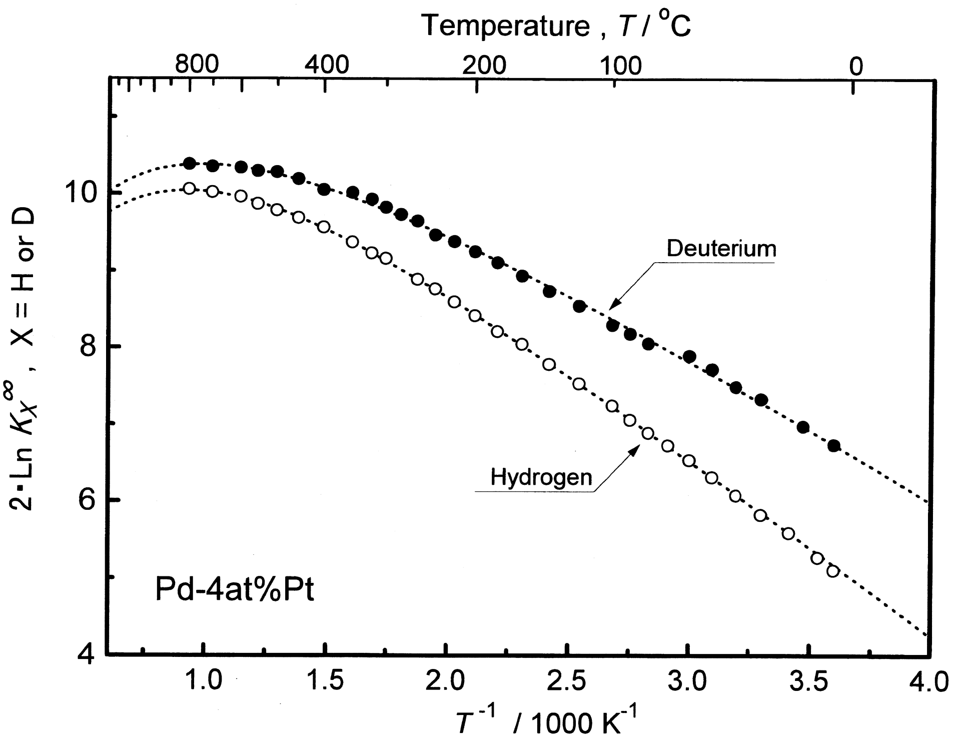

Fig. 5. Temperature dependence of the equilibrium constants (K^∞) of H_2 and D_2 for Pd–4 at.% Pt; the fitting results were shown by dotted lines.

The equilibrium constant at infinite dilution for H_2 was determined from the intersect of the lines with the y-axis in Fig. 4. The equilibrium constant for D_2 was determined similarly. They are plotted in Fig. 5 for the 4 at.% Pt alloy. As seen in the figure, there are apparent curvatures for both isotopes especially at higher temperatures. It is implied that the partial molar enthalpy and entropy are temperature dependent. According to Lässer et al. [10,11], the temperature dependence of the equilibrium constant is as follows:

$$2\ln K^{\infty} = \ln\left(\frac{LT^{7/2}}{1-e^{-J/T}}\right) + \frac{M}{T} - 2\ln\frac{N(1+Ae^{-B/T})}{(1-e^{-C/T})^{3}} - 2\left(\frac{E-1.5C}{T}\right) \qquad (2)$$

The first two terms in Eq. (2) give the standard Gibbs free energy of a hydrogen molecule, where $LT^{7/2}$ is the translational–rotational partition function, J is the Einstein temperature, M is the constant determined by the dissociation energy and the rotational constant of the hydrogen molecule. The third term is the appropriate sum over all possible states of hydrogen dissolved in a metal. The term $(1-e^{-C/T})^{-3}$ is the sum over all vibrational states referenced to the ground state energy if the hydrogen atom behaves as an isotropic, three-dimensional harmonic oscillator with Einstein temperature, C. The term $(1+Ae^{-B/T})$ is a correction term considering all contributions from anharmonic effects, other vibrational manifolds and electronic energy states. The last term $(E-3C/2)$ is the ground state energy of hydrogen dissolved in the metal with respect to atomic hydrogen at rest, where E is the vibrational potential minimum with respect to atomic hydrogen and $3C/2$ is the zero-point energy.

The equilibrium constants at different temperatures were fitted using a non-linear least-squares-fit program, where molecular constants, L, J and M were cited from the literature [10–12], and the constants (A's) determined for Pd by Lässer and Powell [10] are assumed to be valid for the Pd–Pt alloys used in the this study. The evaluated parameters describing the temperature dependence of K^{∞} are summarized in Table 1 along with the applied molecular constants (Table 2). The excellent agreement between the experimentally determined K^{∞}'s and fitting curves was observed not only for 4 at.% Pt alloy, as seen in Fig. 5, but also for other alloys used. Those analyses indicated that the ground state of H in the samples measured from the dissociation limit of 0.5 moles of the isotopes moves up with increasing Pt content in the alloy from 26 945 K (2321.9 meV) for Pd to 26 783 K (2307.9 meV) for 8 at.% Pt. For D the ground state was about $1/\sqrt{2}$ lower than that of H for respective alloys.

Table 1
List of parameters A, B, C and E used to calculate K^{∞} constants with Eq. (2)

X	A	B (K)	C (K)	E (K)	E–1.5C(K)
Pd–5 at.% Pt alloy					
Hydrogen	1.981	2573	655.2	27838	26855
Deuterium	1.933	3920	444.2	27885	27219
Pd–8 at.% Pt alloy					
Hydrogen	1.981	1593	781.6	27955	26783
Deuterium	1.933	1590	543.0	27992	27178

Table 2
List of parameters L, J and M used to calculate the standard Gibbs free energy of 1 mole of diatomic hydrogen gas

Molecule	L ($K^{-7/2}$)	J (K)	M (K)
HH	4.293×10^{-4}	5986	51994.9
DD	2.406×10^{-3}	4307	52888.2
TT	6.582×10^{-3}	3548	53285.6

3.2. Properties of the two-phase region

Isotherms for alloys of different composition are shown in Fig. 6 for hydrogen desorption at 353 K. In comparison with the isotherm for Pd, the equilibrium pressures for the Pd–Pt alloys at a given hydrogen concentration increase with increasing Pt content in the alloys. In addition, the increasing Pt content gives rise to a reduction of the plateau width and an increase in the slope. These mean a decrease in the Gibbs free energy for hydride formation with increasing Pt content.

Although the well-defined plateau was only observed for Pd and 4 at.% Pt alloy, the temperature dependence of the plateau pressure was examined for all alloys at a hydrogen concentration of $x=0.2$. The van't Hoff plots of H_2 and D_2 for alloys with 4, 8 and 10 at.% Pt resulted in good straight lines. The enthalpy and entropy changes obtained are summarized in Table 3. Although the enthalpy and entropy changes for Pd evaluated from the absorption isotherms differed from the values in the literature [14], those determined from the desorption isotherms were in good agreement. As for the alloys, the enthalpy changes determined in this study appear to differ from those reported by Maeland and Flanagan [13]. This is because they evaluated those values electrochemically in the temperature range 273–323 K. As to the effect of alloying, however, the same tendency was observed; namely, the heat of the hydride formation decreased with increasing Pt content in the alloy while the entropy change was kept almost constant.

In addition, the difference in the enthalpy term between H_2 and D_2 was basically the same for all Pt contents. As a result, the ratio of the equilibrium pressures between the hydrogen and deuterium does not change much with Pt concentration. This is shown in Fig. 7, where the P_{D_2}/P_{H_2} ratios observed in the α and (α + β) regions are plotted together against temperature. The equilibrium pressure ratio is naturally temperature dependent, but appears to

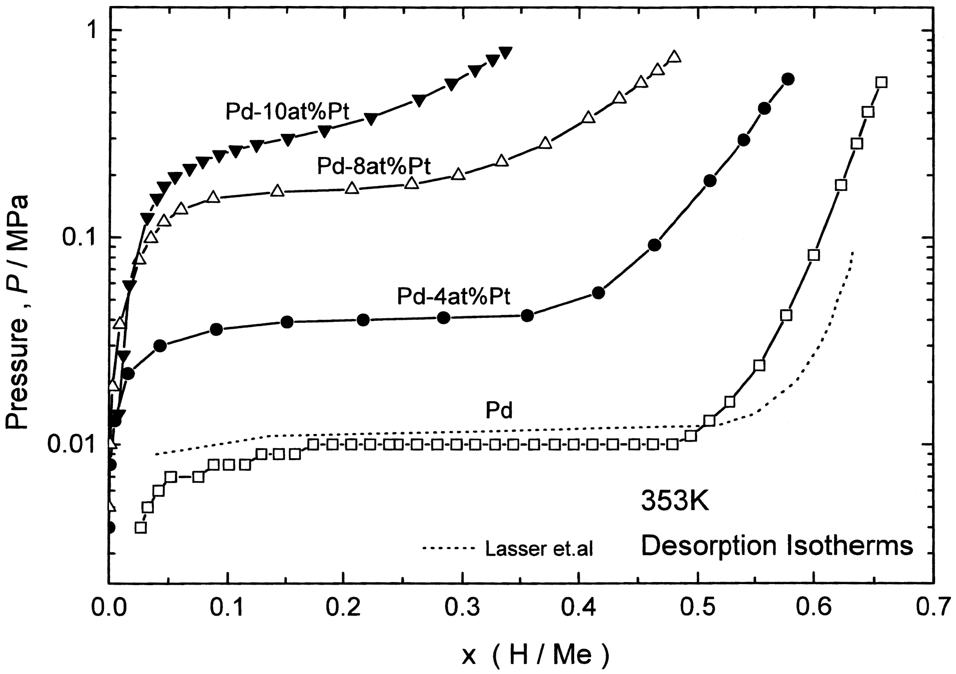

Fig. 6. Comparison of the H_2 isotherms at 353 K for alloys with different Pt contents.

vary little with the alloy composition. This is principally due to the very similar difference in the enthalpies for reacting with H_2 and D_2 and the almost invariable entropy change with the alloy composition.

This means that the separation efficiencies of hydrogen isotopes using the newly developed gas chromatography technique depend greatly on the operation temperature, but does not vary appreciably with the Pt content of the alloy. On the other hand, the heat of the hydrogen absorption and the hydride formation changes extensively with the alloy composition; hence the equilibrium pressures of the isotopes change considerably with alloy composition. On the basis of those facts, one can select the most appropriate alloy as a working material of the chromatograph depending on the required operation conditions, without significant change in the separation efficiency.

4. Conclusions

The absorption–desorption isotherms of hydrogen and

Table 3
$\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transition enthalpies and entropies of the Pd H, Pd D, Pd–Pt H and Pd–Pt D system for absorption and desorption processes, respectively ($X_2 = H_2$ or D_2)

	$\Delta H^{\alpha \rightarrow \beta}$ (kJ/mol X_2)	$\Delta S^{\alpha \rightarrow \beta}$ (J/K mol X_2)	$\Delta H^{\beta \rightarrow \alpha}$ (kJ/mol X_2)	$\Delta S^{\beta \rightarrow \alpha}$ (J/K mol X_2)	Reference
$PdH_{0.2}$	−33.1	−82.2	40.2	94.7	This work
$PdD_{0.2}$	−29.8	−83.2	35.1	91.6	
PdH	−37.4	−92.5	39.0	92.5	Lässer and Klatt [14]
PdD	−33.6	−93.3	35.4	93.4	
PdT	–	–	33.3	91.7	
Pd–4 at.% Pt $H_{0.2}$	−30.9	−82.6	37.4	97.9	This work
Pd–4 at.% Pt $D_{0.2}$	−26.7	−81.6	31.6	93.1	
Pd–8 at.% Pt $H_{0.2}$	−29.4	−87.6	30.7	91.5	This work
Pd–8 at.% Pt $D_{0.2}$	−26.4	−90.4	28.3	96.1	
Pd–10 at.% Pt $H_{0.2}$	−28.9	−91.7	30.7	97.3	This work
Pd–10 at.% Pt $D_{0.2}$	−26.6	−96.5	27.0	97.5	

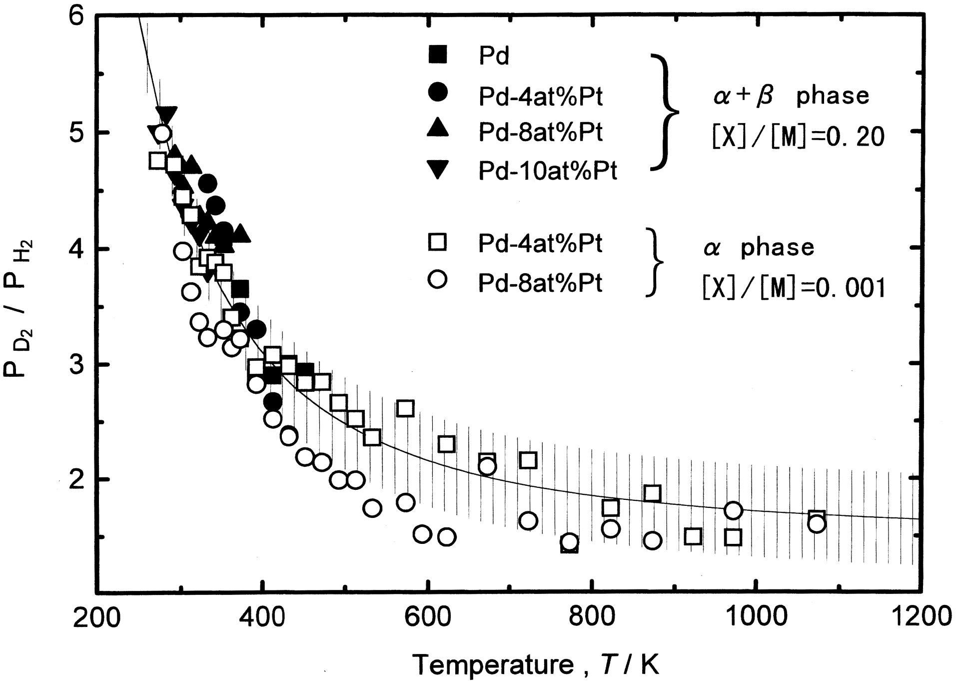

Fig. 7. Temperature dependence of equilibrium pressure ratio between H_2 and D_2 for Pd–Pt alloys.

deuterium for Pd–Pt alloys were studied to search for profitable working materials using the newly developed gas chromatography technique for hydrogen isotope separation. The results of the present study are summarized as follows:

- The equilibrium pressures of the isotopes increased with increasing Pt content in the alloys with a reduction in the plateau width and an increase in the slope. The plateau pressure ratio between H_2 and D_2 at a given temperature does not change much with varying Pt content in the alloys.
- The van't Hoff plot of the plateau pressures showed that the heat of hydride formation decreased almost linearly with the Pt content, whereas the entropy change remained almost constant. However, the difference in the heat of the hydride formation between the two isotopes did not depend much on the alloy composition.
- In the α-phase absorption, strong temperature dependence of the heat and entropy of absorption were observed for all of the alloys used for both isotopes. The analysis of the temperature dependence showed that the ground state of H in the samples referenced to the dissociation limit of 0.5 moles of hydrogen rises with increasing Pt content in the alloy from 26 945 K (2321.9 meV) for Pd to 26 783 K (2307.9 meV) for 8 at.% Pt. For D the ground state was about $1/\sqrt{2}$ lower than that of H for respective alloys.
- On the basis of the present observations, it is highly probable that one can select the most appropriate alloy for use as the working material for the chromatography system, depending on the required operation conditions, without a significant change in the separation efficiency.

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