

# Absorption of Hydrogen Isotopes by Pd-based Alloys

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To find out the most efficient column material for a newly developed gas chromatographic hydrogen isotope separation system, changes in the heat of hydrogen absorption and in the thermodynamic isotope effect with alloy composition were investigated for Pd-based alloys,  $\text{Pd}_{(1-x)}\text{AE}_x$ , where  $\text{AE} = \text{Co, Ni, Cu, Rh, Pd, Ag, Pt, or Au}$ . It was experimentally observed that the heat of absorption decreased with increasing AE content for Co, Ni, Cu, Rh, Pt, and Au, although the extent of the reduction differed from each others. On the other hand, alloying of Ag caused the increase in the heat of absorption. With respect to the isotope effect, variations of the alloying element and the extent of alloying showed no noticeable effect on the isotope effect among the alloys investigated including pure Pd.

Those features were analyzed from electronic structures of the alloys by use of Gaussian 03 and DVX $\alpha$  packages, where the calculations were carried out for small clusters as  $\text{Pd}_{(8-y)}\text{AE}_y$  for the former and  $\text{Pd}_{(14-y)}\text{AE}_y$  for the latter. The *ab initio* calculations showed that the energy of the highest occupied molecular orbital of the clusters changes almost linearly with alloy composition, suggesting that the Fermi energy changes with alloy composition. By assuming the Fermi energies of alloys to be arithmetic means of the Fermi energies of pure Pd and AE, a linear relation was found between the observed heat of absorption and the Fermi energy of the alloys. Vibrational analysis of  $\text{Pd}_{(8-y)}\text{AE}_y\text{-H}$  systems showed that the force constant for the bond between a H and a host metal atoms does not change much irrespective of different alloying element, causing the isotope effect to be almost invariant with alloying element and alloy composition.

**Keywords:** hydrogen absorption, Pd-alloys, heat of absorption, isotope effect, alloying effect

## 1. Introduction

Palladium and its alloys with some transition elements are most attractive for application to column materials of a newly developed gas chromatographic hydrogen isotope separation system[1, 2]. The new separation system can be operated near room temperature without using any replacement gas, as required for replacement chromatography so far developed[3]. Its operation principles are dissociative absorption of hydrogen isotopes by column

materials and the associative desorption of absorbed isotope atoms. For this application, therefore, the heat of hydrogen absorption and the hydrogen isotope effect are of primary importance, where it has been confirmed that the thermodynamic isotope effect predominates over the kinetic one[4, 5, 6]. The temperature at which the column can be operated is principally determined by the heat of absorption, and the thermodynamic isotope effect concerns

with the separation efficiency at a given operation temperature.

As a first step to find out the most effective column material for the separation of hydrogen isotopes, the authors have studied the alloying effect on the heat of hydrogen absorption and the isotope effect for Pd-AE alloys, where AE = Co, Ni, Cu, Rh, Pd, Ag, Ir, Pt, or Au, by measuring absorption and desorption isotherms of protium and deuterium[4, 7]. They are expected to have moderate heat of absorption around 30 kJ/mol(H<sub>2</sub>) and to be highly resistive for surface poisoning by impurity gases.

Along with these measurements, *ab initio* calculations for small clusters such as Pd<sub>(8-y)</sub>AE<sub>y</sub> and Pd<sub>(14-y)</sub>AE<sub>y</sub> were carried out to understand fundamental roles of alloying on the heat of absorption and the isotope effect, by use of Gaussian 03 package[8] for the former and DVX $\alpha$  package[9] for the latter. In the case of former calculations, vibrational analysis of Pd<sub>(8-y)</sub>AE<sub>y</sub>-H systems was also performed.

## 2. Experimental

### 2.1. Materials

The Pd-AE (AE = Co, Ni, Cu, Rh, Pt, or Au) alloys were prepared with argon arc melting. Each material in plate or powder form was purchased from Nirako, and their purity was guaranteed as Pd > 99.9, Co > 99., Ni > 99.7, Cu > 99.9, Rh > 99.9, Pt > 99.98, Au > 99.95 %. The plates were cut to small pieces. These raw materials were weighed to prescribed amounts for preparing a Pd-AE alloy of a given composition. They were set into a sample pot installed in an arc-melting device. After evacuation of the system below  $1 \times 10^{-6}$  Torr, high purity argon was introduced. The discharge of Ar was carried out by applying 20 V in an Ar atmosphere of 0.11 MPa. The arc-melting was repeated five times to obtain an ingot of uniform composition. The composition and crystallinity were examined by radiofrequency inductively coupled plasma atomic emission spectroscopy (ICP) or X-ray fluo-

rescent analysis (XRF) and X-ray diffraction (XRD). Details of the procedures have been described in previous papers[4, 5, 7].

Gases used were purchased from Nihon Sanso. Their purities were guaranteed as 99.9999% (Ar), 99.99999%(H<sub>2</sub>) and 99.6%(D<sub>2</sub>). They were used without further purification.

### 2.2 Apparatus and procedures

Ab- and desorption isotherms of protium and deuterium were measured by use of two different devices, for both of which the constant volume method was applied. The isotherms in a range from  $1 \times 10^3$  to  $1 \times 10^6$  Pa in equilibrium pressure were measured by use of an automatic measuring system, whereas the measurements of the isotherms in a range from  $1.3 \times 10^{-3}$  to  $1 \times 10^5$  Pa were carried out by use of a high vacuum system.

The alloy ingots obtained were filed to powder and the filings below 200 mesh were weighed to 1.5 g for isotherm measurements. The sample powder was activated in each device by vacuum heating at 800°C for one hour for measurements in the low pressure region, and at 250°C for two hours for the high pressure region. Further details of experimentals have been described elsewhere[4, 5, 7].

## 3. Results and Discussion

### 3.1. Alloying effect on the heat of absorption

Alloying effect on the hydrogen absorption is evaluated from the heat of absorption, since the entropy change for the absorption does not differ much for various hydrogen absorbing materials. **Figure 1** shows as example the desorption isotherms of H<sub>2</sub>, observed for Pd-4at%Pt alloy at a temperature range from 60 to 160°C. It is seen that the equilibrium pressure increases and the plateau region becomes narrower with increasing temperature, but the plateau was kept rather flat in this temperature range. Those properties are expected to give good self-developing chro-

matograms of hydrogen isotopes in the separation column. **Figure 2** compares the desorption isotherms of  $H_2$  for Pd-Pt alloys of different compositions at 333 K as referenced to pure Pd, showing as way of example the alloying effect on the isotherms, namely the enthalpy change for hydrogen absorption. The equilibrium pressure increases with increasing extent of Pt-alloying, indicating that the heat of hydrogen absorption decreases with increasing content of Pt in the alloys.

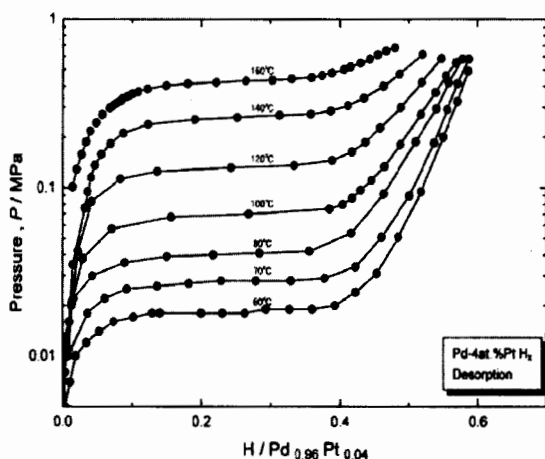


Fig. 1: Desorption isotherms of  $H_2$  for Pd-4at%Pt at different temperatures

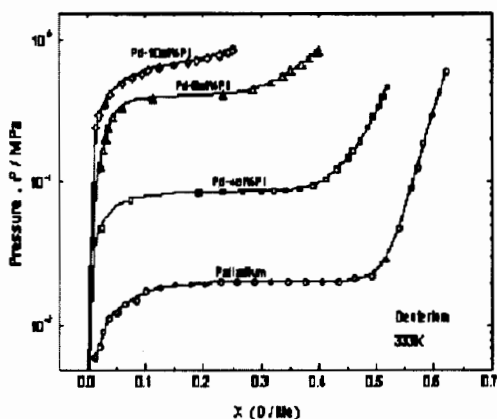


Fig. 2: Alloying effect on the isotherms of  $H_2$  for Pd-Pt alloys

The heats of absorption of protium and deuterium were determined from the temperature dependence of the isotherms by plotting  $\ln P_{eq}$  vs  $1/T$  at a hydrogen concentration of  $[Q]/[Me]=0.2$  for all the ma-

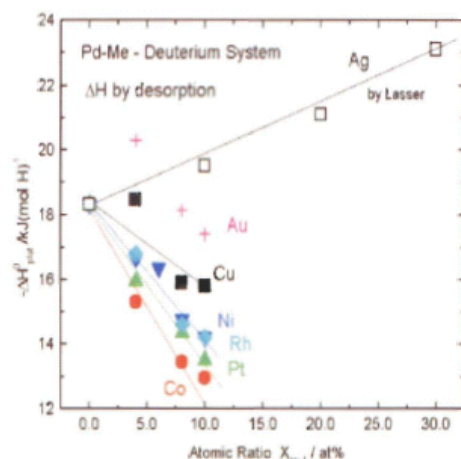


Fig. 3: Change in the heat of  $D_2$  absorption by Pd-AE with alloy composition

terials used, where Q represents H or D, and Me indicates respective alloys. **Figure 3** shows the results of such evaluation, where the enthalpy changes for hydrogen absorption determined from desorption isotherms are plotted against alloy composition for Pd-AE. Data obtained for Pd-Ag by Lässer[10] are also plotted together. This figure shows a trend that the heat of absorption decreases by alloying with Co, Ni, Cu, Rh, Pt and Au, and the extent of the reduction is approximately linear to the alloy composition, although there appeared data scattering as 4%Cu and 4%Au alloys. On the other hand, Lässer's results show that the heat of absorption increases almost linearly with increasing fraction of Ag. These features do not agree with a well-known empirical relation between the heat of hydrogen absorption and the size of hydrogen capturing site[11], because the lattice constant is almost invariant for Pd-Pt alloys irrespective of the composition, decreases by alloying with Co, Ni, Cu and Rh, and increases for Ag and Au[12, 13].

From another point of view, enough evidence has been found for clear correlations between the heat of hydrogen absorption and electronic energy state of host alloys[14]. To examine the role of electronic factor, *ab initio* calculations were carried

out for small clusters such as  $\text{Pd}_{(8-y)}\text{AE}_y$  and  $\text{Pd}_{(14-y)}\text{AE}_y$  by use of Gaussian 03 and/or DVX $\alpha$  packages in the present study. The electronic energies of the highest occupied molecular orbitals (HOMO) were calculated by DVX $\alpha$  for clusters of  $\text{Pd}_{(14-y)}\text{AE}_y$  such as shown in **Fig.4**, which corresponds to the  $\text{Pd}_{12}\text{Ni}_2$  cluster. To increase the Ni-content, Pd atoms on the corners were replaced by Ni.

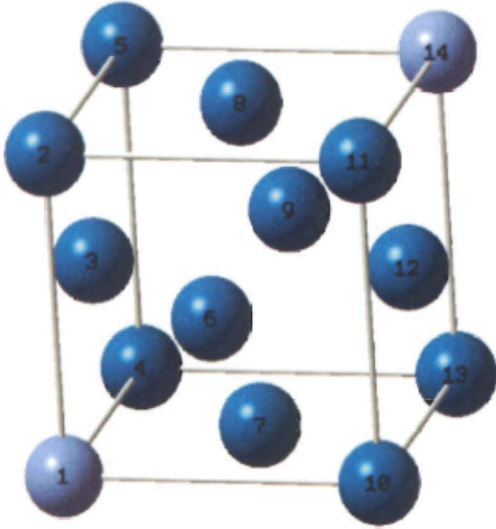


Fig. 4:  $\text{Pd}_{12}\text{Ni}_2$  cluster for DVX $\alpha$  calculation

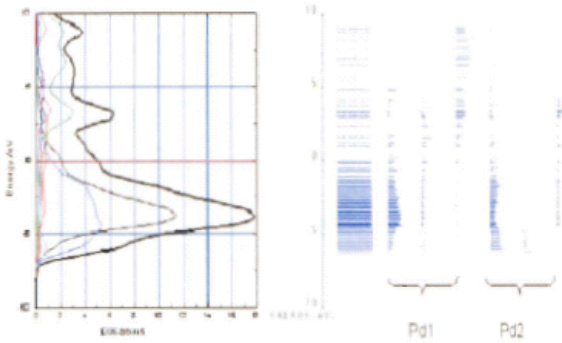


Fig. 5: DOS of  $\text{Pd}_{14}$

**Figures 5 and 6** show calculated density of states (DOS) of  $\text{Pd}_{14}$  and  $\text{Pd}_{12}\text{Ni}_2$  clusters. In these figures, the ordinate represents electron energy in eV. As for DOS in the left of each figure, the abscissa gives DOS in arbitrary unit. The bar-maps at the right are drawn to show

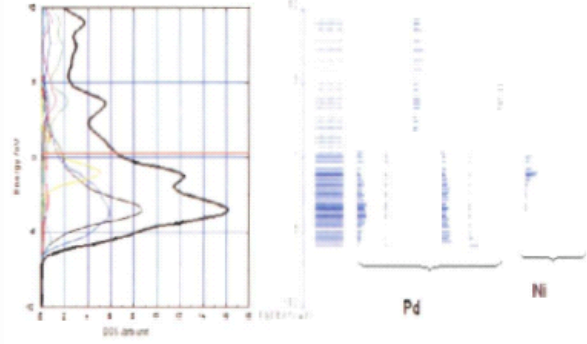


Fig. 6: DOS of  $\text{Pd}_{12}\text{Ni}_2$

more clearly the contributions of molecular orbitals. The barmap at the right of Fig.5 represents the contributions of 4d, 5s and 5p orbitals of Pd atoms located at the corner (denoted as Pd1) and the face-center of the cluster (Pd2). In the bar-map of Fig.6, the contribution of 3d, 4s and 4p orbitals of Ni atoms, locating at the corner, are also shown. These figures show that the hybrid orbitals of Ni-3d, 4s and 4p contributes to the total DOS of  $\text{Pd}_{12}\text{Ni}_2$  to lift up its HOMO level, because of their higher energy states in comparison with those of Pd. The results of calculation for  $\text{Pd}_{(14-y)}\text{AE}_y$ , where  $y = 2 \sim 8$ , are shown in **Fig.7**. Although the results scatter in some extent, it appears that the HOMO level increases with increasing Ni-content in the clusters. Similar calculations were done for other alloy systems, and almost linear correlations between HOMO level and cluster composition were found.

The HOMO levels of the clusters thus calculated are considered to be correlated with the Fermi energies of respective crystalline alloys. The Fermi energies of pure metals and alloys could not be calculated in the present study. According to the results shown in **Fig.7**, however, it is considered that  $E_f$  of  $\text{Pd}_{(1-y)}\text{AE}_y$  alloys ( $0 \leq y \leq 1$ ) can be approximated by simple arithmetic means of Fermi energies of constituent elements as

$$E_f(\text{Pd}_{1-y}\text{AE}_y) = (1 - y)E_f(\text{Pd}) + yE_f(\text{AE}), \quad (1)$$

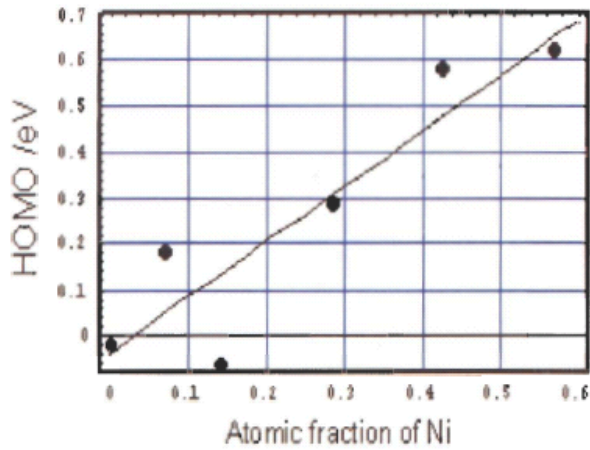


Fig. 7: Change in HOMO level of  $\text{Pd}_{(14-y)}\text{Ni}_y$  clusters with composition

where  $E_f(\text{Pd})$  and  $E_f(\text{AE})$  are the Fermi energies of pure Pd and alloying element AE, respective, and  $y$  the atomic fraction of AE in the alloy. The Fermi energies of elemental solids are given in the handbook by Papaconstatopoulos[15], and hence  $E_f$  of an alloy of a given composition can be obtained easily.

Figures 8 and 9 show the plots of

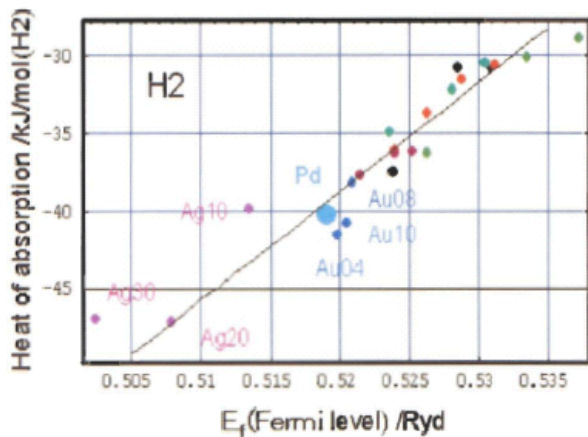


Fig. 8: Heat of protium absorption vs  $E_f$  of Pd-alloys

observed heat of protium absorption and of deuterium absorption vs the Fermi energy of Pd-alloys evaluated by Eq.(1) using the tabulated values of  $E_f$  for respective pure elements. Although scattering of data appears in some extent, the heat of absorption decreases almost linearly with the Fermi energy of alloy for both protium

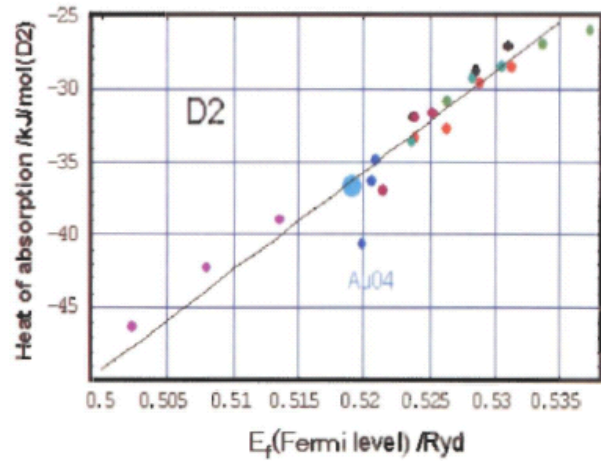


Fig. 9: Heat of deuterium absorption vs  $E_f$  of Pd-alloys

and deuterium. This relation is similar to the semi-empirical relation by [11, 16] and analogous to that for evaluating bonding energy of molecules by means of electronegativity proposed by Pauling[17] and a similar relation has been found for hydrogen absorption by various hydrogen storage materials[18, 19].

### 3.2. Isotope effect on the heat of absorption

Figure 10 is an example of the isotope

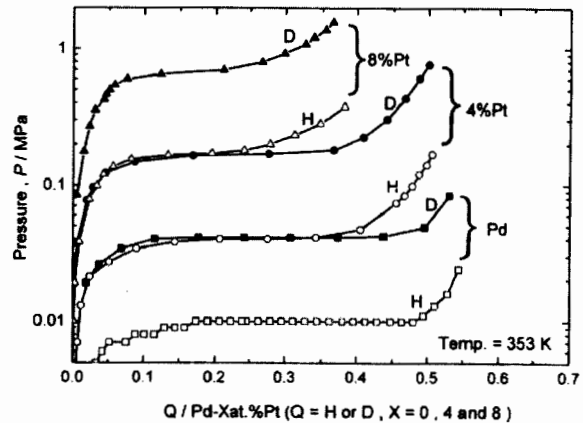


Fig. 10: Desorption isotherms of  $\text{H}_2$  and  $\text{D}_2$  at 353 K for Pd-Pt alloys

effect for hydrogen absorption which shows the difference in the desorption isotherms of  $\text{H}_2$  and  $\text{D}_2$  observed at 353 K for Pd-Pt alloys. As mentioned above, the equilibrium pressure of protium was lifted up by alloying with Pt, that of deuterium was also increased with alloying. It should be noted, however, that the isotope effect, as

measured by  $P_{D_2}/P_{H_2}$ , was kept almost constant around 4, being almost invariant with the alloying irrespective to the alloy composition.

Since hydrogen molecules are dissociatively absorbed by the alloys and a hydrogen atom is trapped in an octahedral site of Pd-alloys, it is considered that the isotope effect principally arises from vibrational partition functions of the trapped isotopes.

Figure 11 summarizes the results of

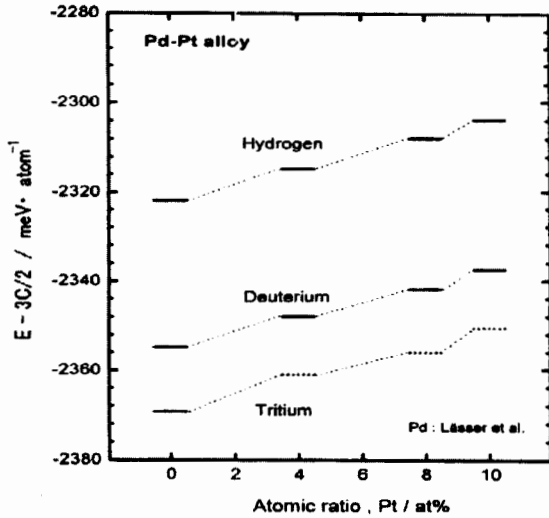


Fig. 11: Isotope effect on vibrational level of Q for Pd-Pt alloys

analyses of the absorption isotherms in  $\alpha$ -phase regions under the above mentioned assumption[4], where the zero-point vibrational energy levels of Q for respective alloys are plotted against Pt-composition in Pd-Pt alloys with reference to the results by Lässer for pure Pd. It is mentioned here that isotherms of tritium were only observed for pure Pd by Lässer in this series of materials. In this figure, it is seen that the vibrational energy levels of protium and deuterium rise together with increasing Pt-content in the alloy, in accordance with the observations shown in Figs.3 and 11. It should be notice here that the difference in the energy levels between protium and deuterium were almost constant around 1.4 for all the Pd-Pt alloys studied and Pd as well, and that between protium

and tritium for Pd was about 1.7. Similar features have been observed for other systems as reported previously[4, 5, 7] or will be reported separately. These observations suggest that the isotope effect on the hydrogen absorption roughly obeys square root law,  $\propto \sqrt{m_H/m_Q}$ , where  $m_H$  and  $m_H$  are the mass of protium and its isotope as deuterium or tritium. The dotted lines for PdPt-T systems were drawn by assuming the square root law.

The *ab initio* calculations for the isotope

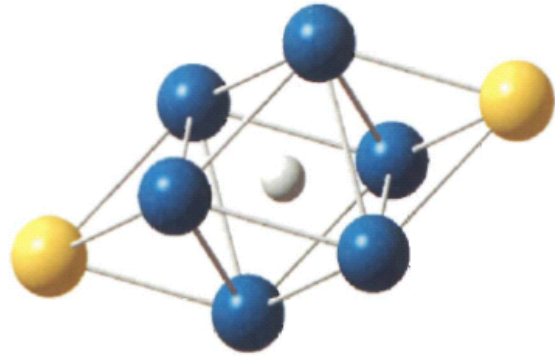


Fig. 12: Cluster model for vibrational analysis

effect was carried out for clusters of  $Pd_8-Q$  and  $Pd_6AE_2-Q$ , where AE is Co, Ni, Cu, Rh, Ag, Pt and Au, and Q denotes H, D or T, by Gaussian 03. The cluster used is represented by Fig.12, where Pd-atoms make the octahedron and the two AE-atoms are located at the diagonal positions of the cluster. Figs.13 and 14 are schematic potential wells calculated for  $Pd_8H$  cluster and for Pd-H determined for Pd-H( $\alpha$  phase) by Lässer[10], respectively. According to Lässer, the difference in the vibrational levels between protium and deuterium was 0.030 and that between deuterium and tritium 0.013 eV. The cluster calculation gave the difference of 0.033 eV between H and D and that of 0.009 eV between D and T.

Figures 15 and 16 are the schematic representations of potential wells determined from the isotherms for Pd-4at%Pt

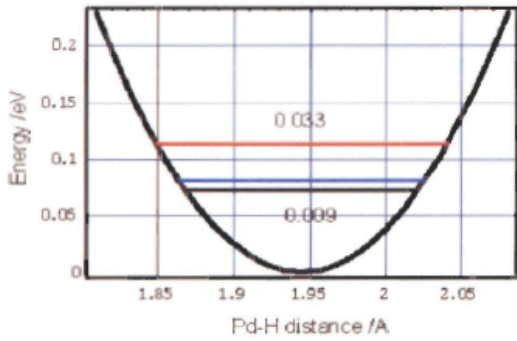


Fig. 13: Schematic potential well for Pd<sub>8</sub>-H cluster

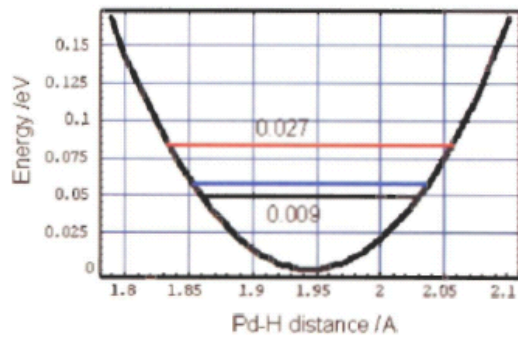


Fig. 15: Potential well for Pd-4at%Pt-H determined from isotherms

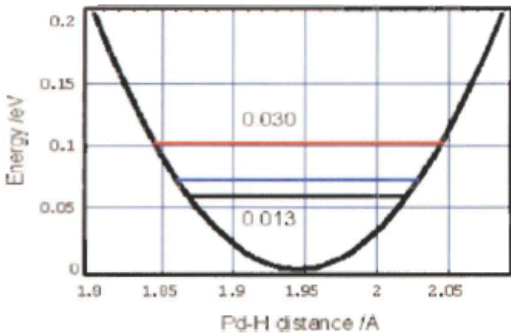


Fig. 14: Potential well for Pd-H determined from isotherms

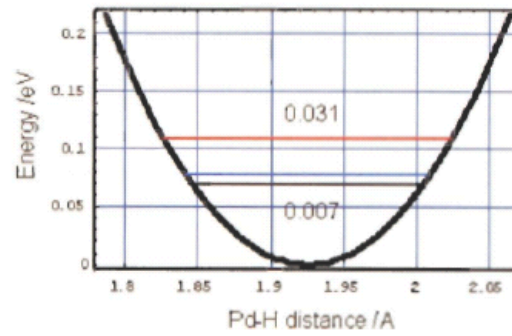


Fig. 16: Potential well for Pd<sub>6</sub>Pt<sub>2</sub>-H determined from isotherms

and those calculated for Pd<sub>6</sub>Pt<sub>2</sub> cluster. The experimental results gave the difference of 0.027 eV between H and D, whereas it was calculated to be 0.031 eV. The difference between D and T was evaluated to be 0.009 and calculate as 0.007 eV. It appears that the cluster calculation resulted in a little larger difference between H and D, and a smaller values between D and T in comparison with those determined from experimental results. This trend was also observed for other alloy systems. According to all the calculations for Pd<sub>6</sub>AE<sub>2</sub>Q systems, there appeared a trend that the separation of two given Pd atoms increases from Pd<sub>6</sub>Cu<sub>2</sub>Q  $\approx$  Pd<sub>6</sub>Ni<sub>2</sub>Q to Pd<sub>6</sub>Ag<sub>2</sub>Q, which roughly agree with the observed feature for the change in the lattice constant with alloying. In addition, it was suggested by the calculations that the difference in the enthalpies between Pd<sub>6</sub>AE<sub>2</sub>H and Pd<sub>6</sub>AE<sub>2</sub>D increases with increasing Pd-Pd separation, implying that the isotope effect on hydrogen absorption is larger for the alloys such as Pd<sub>6</sub>Cu<sub>2</sub> and Pd<sub>6</sub>Ni<sub>2</sub> in

comparison with Pd<sub>6</sub>Au<sub>2</sub> and/or Pd<sub>6</sub>Ag<sub>2</sub>. In comparison with the difference in the binding energy of about 0.08 eV between H<sub>2</sub> and D<sub>2</sub>, the differences in the energy states of absorbed H and D were so small as around 0.005 eV for Pd<sub>6</sub>Cu<sub>2</sub> and Pd<sub>6</sub>Ni<sub>2</sub>, and about 0.03 eV for Pd<sub>6</sub>Au<sub>2</sub> and/or Pd<sub>6</sub>Ag<sub>2</sub>. Accordingly the isotope effect on hydrogen absorption does not change much by alloying with the elements selected in the present study. This feature agree fairly well with the observation that the isotope effect was almost the same for different alloying elements irrespective to their composition within a frame of the present investigation.

#### 4. Conclusion

Pd-AE (AE = Co, Ni, Cu, Rh, Ag, Pt, or Au) alloys were subjected to measurements of ab-/desorption isotherms of protium and deuterium to search for suitable column materials for the newly developed gas chromatographic isotope separation system. In addition, *ab initio* calcula-

tions by Gaussian03 and DVX $\alpha$  were carried out to understand the role of alloying for affecting the stability of hydrogen in the alloys and the isotope effect by adopting small clusters such as Pd<sub>(8-y)</sub>AE<sub>y</sub> and/or Pd<sub>(14-y)</sub>AE<sub>y</sub> as models of alloys.

It was observed that the alloying with Co, Ni, Cu, Rh, and Pt caused to decrease the heat of absorption with increasing extent with increasing AE composition, whereas the heat of absorption was increased by alloying with Ag. Despite such change in the heat of absorption, however, the isotope effect was almost invariant with the alloying elements and composition.

The *ab initio* calculations showed that the highest occupied level of clusters changes almost linearly with increasing content of alloying element, suggesting the change in the Fermi energy with alloying element and composition. By assuming the Fermi energy of the alloys to be approximated by arithmetic means of those of pure substances, it was found that the heat of absorption changes almost linearly with the Fermi energy of alloys. The *ab initio* calculations also indicated that the extent of isotope effect is larger for the alloys such as Pd<sub>6</sub>Cu<sub>2</sub> and Pd<sub>6</sub>Ni<sub>2</sub> in comparison with Pd<sub>6</sub>Au<sub>2</sub> and/or Pd<sub>6</sub>Ag<sub>2</sub>. But since the differences were so small as around 0.005 eV for Pd<sub>6</sub>Cu<sub>2</sub> and Pd<sub>6</sub>Ni<sub>2</sub>, and about 0.03 eV for Pd<sub>6</sub>Au<sub>2</sub> and/or Pd<sub>6</sub>Ag<sub>2</sub>, the isotope effect does not change much by alloying with the elements selected in the present study. This feature agrees fairly well with the observation that the isotope effect was almost invariant for different alloying elements, irrespective to their composition.

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