

## Monte Carlo simulation of hydrogen absorption in palladium and palladium–silver alloys

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### Abstract

A modified Monte Carlo (MC) simulation was performed to investigate the hydrogen absorption behavior in Pd and Pd–Ag alloys of the composition Pd<sub>x</sub>Ag<sub>1-x</sub> ( $x = 0.7$ – $0.8$ ) under H<sub>2</sub> pressure (0.1 MPa) at different temperatures. The present method employed can consider the dissociative adsorption of hydrogen molecule and the subsequent absorption of hydrogen atom by formalizing the relationship between the pressure of hydrogen molecule and hydrogen atom. The potential parameters were determined to reproduce the solution enthalpy of hydrogen in pure metals. The results are in good agreement with experimental findings as well as previous theoretical studies. We confirmed that our method is useful to simulate the absorption of hydrogen in metals and alloys.

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### 1. Introduction

The properties of hydrogen in metals are important in describing many phenomena such as heterogeneous catalysis, purification of hydrogen by membranes, and storage of hydrogen in metal hydrides [1–6]. However, a detailed understanding of metal–hydrogen systems is required, in particular, for the development of membrane reactor and fuel cell technologies. It is well known that Pd has a special tendency to absorb hydro-

gen compared to many other metals and hence Pd–H system has been investigated extensively [1–6]. On the other hand, Pd and its alloys have been known for their hydrogen separation. Of the Pd alloys, Pd–Ag is by far the most studied [7]. While Pd readily absorbs large amounts of hydrogen at room temperature but hydrogen is practically insoluble in Ag. Despite this, the solubility of hydrogen is larger in Pd–Ag alloys. Further, Pd–Ag alloy membranes have high-selectivity for hydrogen permeation and hence suitable for hydrogen selective membranes. In this regard, the understanding of hydrogen permeation in Pd–Ag alloy is extremely important.

On the other hand, in recent years, computational chemistry has been recognized as a powerful method to design and develop new materials as well as to

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understand the mechanism of the interactions for the various processes at the atomistic level by taking advantage of the tremendous progress made on both the theory and the computational speed. Several theoretical methods such as molecular dynamics (MD), Monte Carlo (MC), quantum chemical calculation, etc. have been employed to extract such information. Concerning theoretical studies on metal–hydrogen systems, the first-principle calculations based on the density functional theory (DFT) have been performed for Pd–Ag–H system with the aim to understand the properties like the energetics of the hydrogen absorption, the energetic preference of hydrogen site, equilibrium lattice constant, etc. [8]. Romanowski et al. [9] have also studied the interaction of hydrogen in various transition metals and their alloys by DFT. Although, the first-principle calculations are quite useful to investigate the metal–hydrogen systems, due to its accuracy and reliability, it may, however, force us to use extremely small cluster models owing to the exorbitant computation time. Thus, it is not attractive for the real systems involving larger models such as the simulation of the hydrogen storage processes in metals and alloys. Thus, a large-scale simulation method is imperative to elucidate the absorption behavior of hydrogen into the pure metals and their alloys. Hence, in the present study, we applied our modified MC program, which can analyze systems having several atoms, to simulate hydrogen absorption in Pd and Pd–Ag alloys. At this juncture, it is also to be noted here that the regular MC program cannot consider such an option, and thus forms this simulator as the first of its kind to calculate precisely the hydrogen sorption behavior in metal and alloy systems.

## 2. Computational details

### 2.1. MC method

The equilibrium absorption of hydrogen in metals and alloys may be calculated by the grand-canonical Monte-Carlo (GCMC) method, employing our originally developed GCMC simulator “MONTA” [10]. However, the conventional as well the GCMC cannot treat the dissociative adsorption of hydrogen molecule and the subsequent absorption of hydrogen atom.

Therefore, we have improved our GCMC program [10], which can take into account of both the dissociation of hydrogen molecule and the absorption of hydrogen atom into the metal/alloy lattice. The algorithm to keep the chemical potential fixed is same as conventional GCMC [11].

In the GCMC simulation, the amount of absorption can be determined by specifying the chemical potential ( $\mu$ ) and the temperature ( $T$ ) of the simulation box. Further, the chemical potential can be related to the pressure of hydrogen molecule. In the gas phase, the chemical potential of the hydrogen molecules equals to that of hydrogen atoms at the equilibrium state, and is expressed as

$$\mu_{\text{H}} = \frac{1}{2}\mu_{\text{H}_2} \quad (1)$$

Accordingly, the following relationship between the pressure of hydrogen ( $p_{\text{H}_2}$ ) molecule and hydrogen atom ( $p_{\text{H}}$ ) is obtained:

$$\frac{p_{\text{H}_2}}{p^0} = \frac{1}{K_{\text{p}}} \left( \frac{p_{\text{H}}}{p^0} \right)^2 \quad (2)$$

where  $p^0$  is the standard pressure and  $K_{\text{p}}$  the equilibrium constant. The temperature dependency of  $K_{\text{p}}$  is determined by van't Hoff equation:

$$\frac{d \ln K_{\text{p}}}{dT} = \frac{\Delta H^0}{RT^2} \quad (3)$$

Now, we can simulate the absorbed hydrogen atoms in metals and alloys by using the relationship between the pressure of hydrogen molecule and hydrogen atom in gas phase.

### 2.2. Pd and Pd–Ag alloy models

We employed a  $4 \times 4 \times 4$  super-cell Pd having a face centered cubic structure and a unit cell dimension of 3.89 Å. A total of 256 Pd atoms were considered in this model. The Pd–Ag alloy model ( $\text{Pd}_x\text{Ag}_{1-x}$ ,  $x = 0.7\text{--}0.8$ ) was obtained by the substitution of Ag for Pd in the lattice. It is also noteworthy here that the hydrogen concentration considered in these systems is very low ( $\ll 0.1$ ). It is, however, important to note that, in this simulation, the lattice expansion and the associated strain around the absorbed hydrogen atom were ignored.

Table 1  
Parameters for different interatomic potentials

Atom pair	$D$ (kJ/mol)	$r_e$ (Å)	$\gamma$ (Å <sup>-1</sup> )
H–H	0.1848	2.886	11.429
Pd–H	17.3000	1.940	4.300
Ag–H	6.4000	2.040	3.000

### 2.3. Interatomic potential

In the MC simulations, the interaction between atoms is represented by the Morse-type function, which is expressed as

$$U_{ij} = D[x^2 - 2x], \quad x = \exp\left[-\frac{\gamma}{2}\left(\frac{r_{ij}}{r_e} - 1\right)\right] \quad (4)$$

where  $r$  is the interatomic distance,  $D$  the well depth,  $r_e$  the equilibrium separation, and  $\gamma$  an adjustable parameters, which determines the potential range. The potential parameters were determined so as to reproduce the experimental data including the heat of dissolution of hydrogen in metals. The various parameters, viz.,  $D$ ,  $r_e$  and  $\gamma$ , were fitted so as to reproduced the data of hydrogen solubility and heat of solution. Table 1 summarizes the various parameters employed in the present investigation.

### 2.4. Theoretical estimation based on Sieverts' law

It is well known that the absorption of hydrogen follows Sieverts' law at low hydrogen concentration as per the following relation:

$$\sqrt{\frac{p}{p^0}} = K_S x \quad (5)$$

where  $p$  is the pressure of hydrogen,  $p^0$  the standard pressure,  $K_S$  the Sieverts' constant, which is dependent on temperature ( $T$ ):

$$\ln K_S = -\frac{\Delta S_s}{R} + \frac{\Delta H_s}{RT} \quad (6)$$

where  $\Delta S_s$  and  $\Delta H_s$  are the solution entropy and enthalpy of hydrogen in the metal, respectively, and  $R$  the gas constant. Theoretical values were estimated by using above equation.

## 3. Results and discussion

### 3.1. Validity of the new simulator

Fig. 1 shows the temperature dependent hydrogen solubility in Pd and Ag under a H<sub>2</sub> pressure of 0.1 MPa from MC calculations and from estimations based on the Sieverts' law. The gradient is corresponding to the solution enthalpy of hydrogen in the pure metal. The calculated values for the solution enthalpy of hydrogen in Pd and Ag are  $-9.51$  and  $67.7$  kJ/mol H, respectively. The values are in excellent agreement with experimental values of  $-10$  and  $68$  kJ/mol H, respectively [7]. Thus, our method reproduces the solution enthalpy of hydrogen in Pd and Ag. Fig. 2 depicts the pressure–composition isotherms of Pd–H system determined by MC simulation as well as by the application of Sieverts' law. As can be seen from this figure that the isotherms obtained by both these methods are in excellent agreement with each other.

### 3.2. Palladium–hydrogen system

The absorption of hydrogen in Pd at different temperatures, viz., 473–773 K, under H<sub>2</sub> pressure of 0.1 MPa was calculated by MC method. The distribution of the absorption energy of the hydrogen in Pd is presented in Fig. 3. It is evident from the figure that the hydrogen atoms possess two different states in Pd lattice. One of them is energetically lower (more negative absorption energy) and hence is more stable than the other energetically higher (less negative absorption energy). In addition, we have also analyzed these two states, i.e., energetically lower ( $-17$  kJ/mol H) and higher ( $-2$  kJ/mol H), by the radial distribution function (RDF) and the result is shown in Fig. 4. It was found that the distance between the hydrogen atom (at lower state) and its nearest Pd atoms is about  $1.45$  Å, while it is  $1.87$  Å for the hydrogen atom at higher state. In addition, we can also visualize the distribution of the hydrogen atom position the two different states, and Fig. 5 illustrates the location of hydrogen atoms in the Pd. From the foregoing results and in conjunction with Fig. 3, it can be deduced that the energetically lower state hydrogen atoms occupy the octahedral sites (see Fig. 5a) and that the energetically higher one prefers to occupy the tetrahedral sites (see Fig. 5b). It is also clear from these results that, in

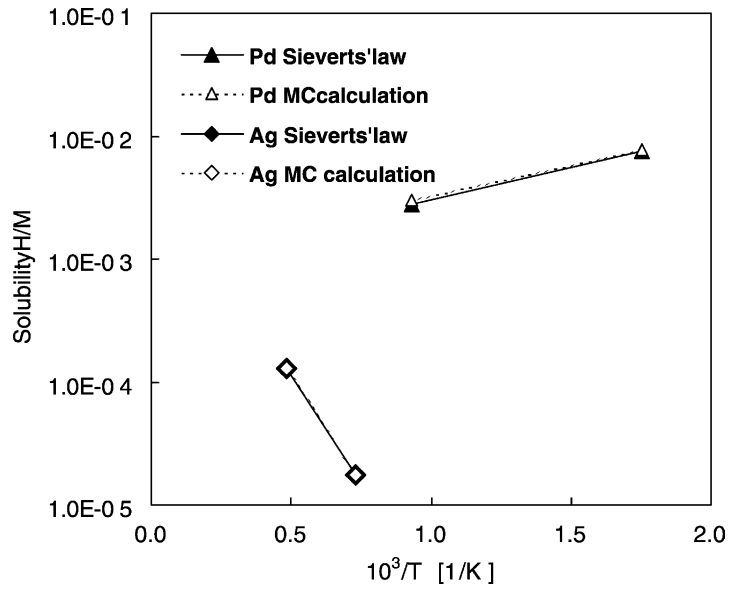


Fig. 1. Solubility of hydrogen in different pure metals.

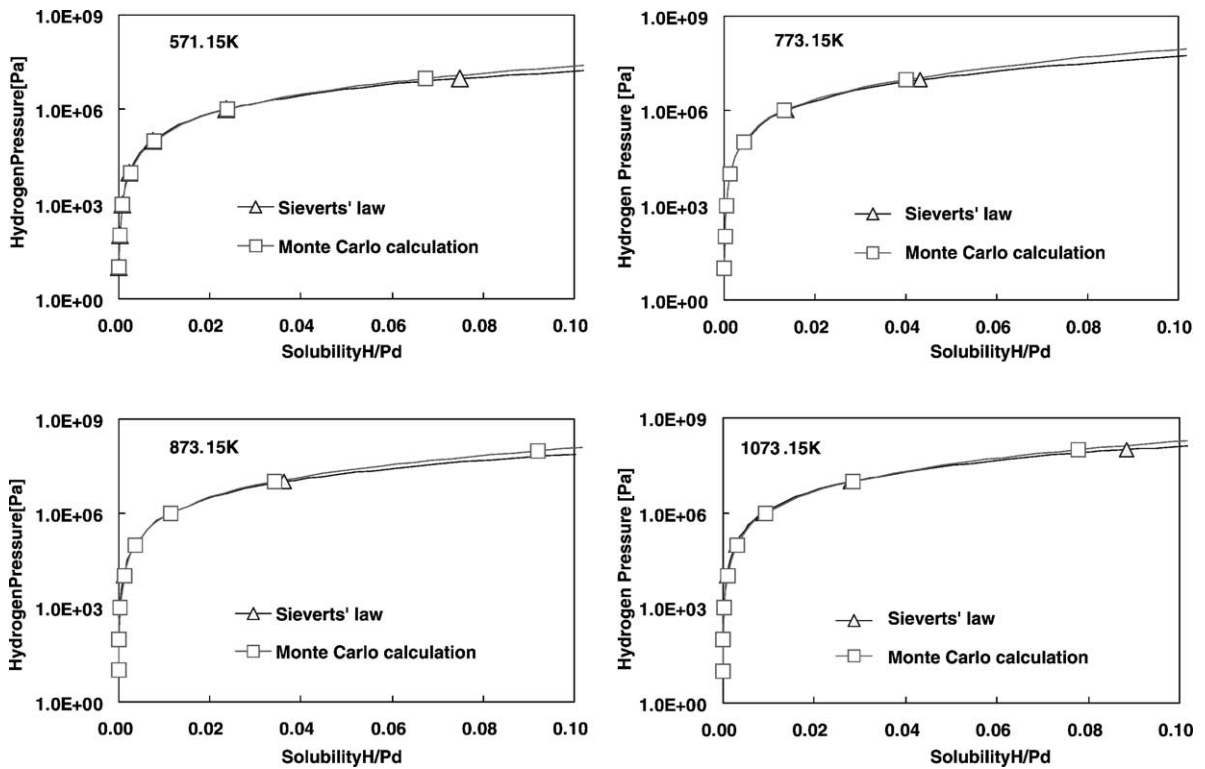


Fig. 2. Pressure-composition isotherms of Pd-H system at different temperatures.

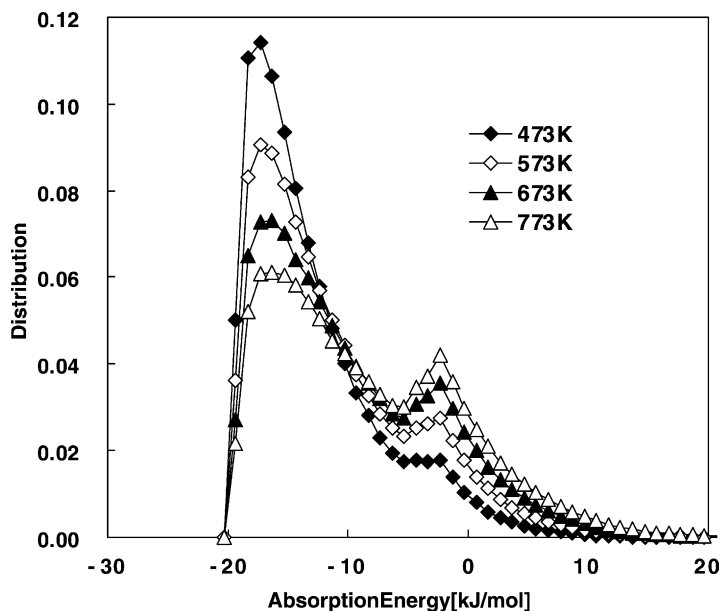


Fig. 3. Absorption energy distribution of hydrogen in palladium ( $p_{\text{H}_2}$ : 0.1 MPa).

the case of Pd, the octahedral site is more preferable than the tetrahedral site, especially at the lower temperature, which is consistent with the experimental data in which mainly occupies octahedral sites [1].

### 3.3. Pd–Ag alloy–hydrogen system

We have also applied our MC method to the investigation of hydrogen absorbed in  $\text{Pd}_x\text{Ag}_{1-x}$  with

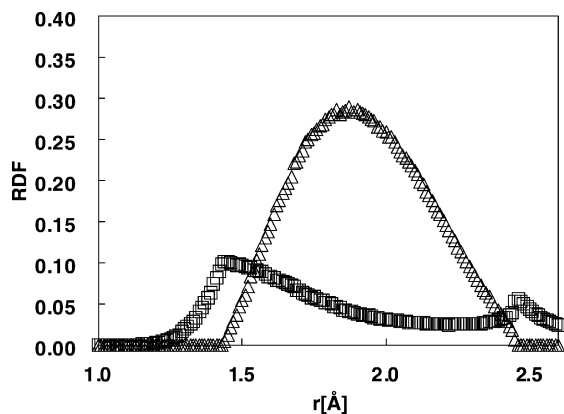


Fig. 4. RDF of the energetically lower ( $\Delta$ ) and higher ( $\square$ ) states (cf. Fig. 3) in Pd and H system.

$x = 0.7\text{--}0.9$  in the temperature range of 473–773 K under  $\text{H}_2$  pressure of 0.1 MPa. For a comparison, we have also included Pd–H system. Fig. 6 shows the hydrogen distribution in Pd metal and in  $\text{Pd}_{0.8}\text{Ag}_{0.2}$  alloy at 473 K. It can be seen from this figure that the distribution of hydrogen in the Pd–Ag alloy is disordered due to the presence of Ag (see Fig. 6b) while for Pd, it is highly ordered (see Fig. 6a). Thus indicating the effect of Ag on the location of hydrogen in the Pd–Ag lattice. On the other hand, we have also analyzed the RDFs of Pd–H and Ag–H in Pd–Ag alloy, and the result is presented in Fig. 7. It is clear from this figure that the intensity of the first peak due to Pd–H is much higher than that for Ag–H. Further, it can be noted that the position of peaks is nearly the same as that in the case of pure Pd (see also Fig. 4) implying that the hydrogen atoms occupy mainly the octahedral sites. This observation is consistent with the DFT studies by Løvvik and Olsen [8], who have suggested that the octahedral site is preferred when most of the neighboring consisting of Pd atoms. Furthermore, it was also found that the nearest distance of Ag–H is shorter than that of Pd–H signifying that the hydrogen atom in contact with Ag atom may occupy the energetically higher site, viz., tetrahedral site. A similar observation was

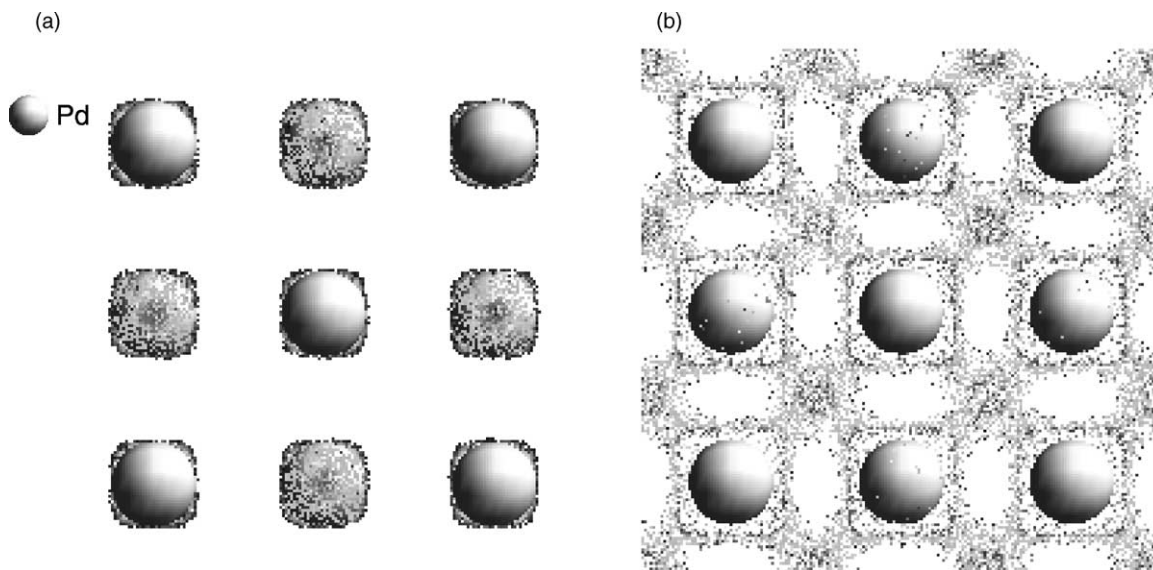


Fig. 5. Distribution of hydrogen-Pd: (a) lower state (octahedral site); (b) higher state (tetrahedral site).

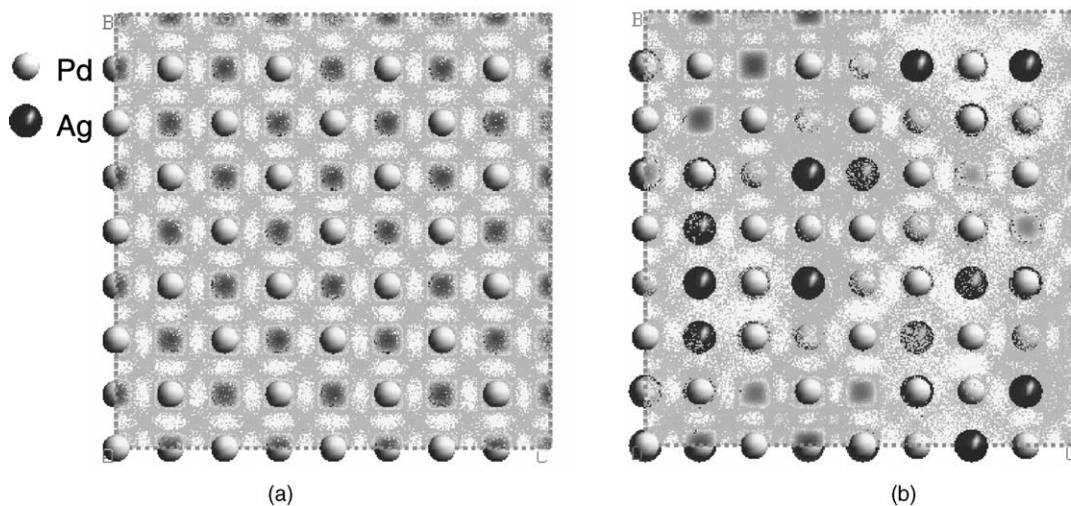


Fig. 6. Distribution of hydrogen in (a) Pd and (b) Pd<sub>0.8</sub>Ag<sub>0.2</sub> at 473 K.

also noted for the other compositions, viz., Pd<sub>x</sub>Ag<sub>1-x</sub> ( $x = 0.7$  and  $0.9$ ).

Fig. 8 shows the distribution of absorption energy of the hydrogen atoms in Pd–Ag alloys at various temperatures. As can be seen from this figure that, at a given temperature, the distribution becomes broader with the increase of Ag content in alloy along with a

shift in the absorption energy (more negative value). Such a broad distribution can also be noticed when the temperature is increased (cf. Fig. 8). In addition, the increase of temperature also results in the change in the intensity of the low- and high-energy states in the alloy suggesting that the increase of Ag as well as the temperature greatly affects the hydrogen absorption

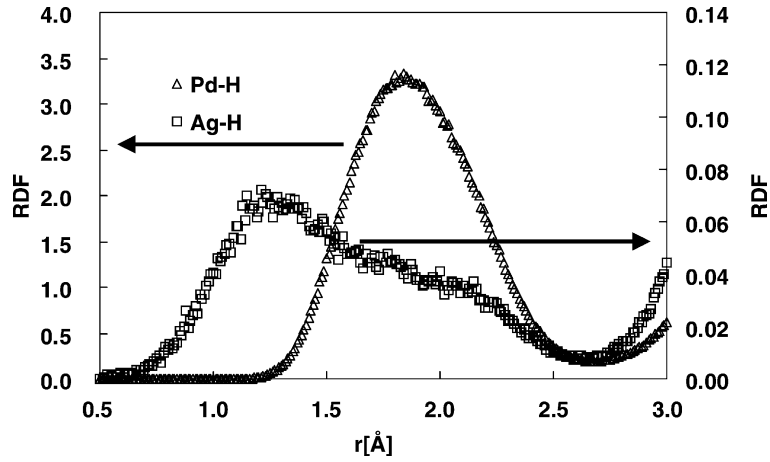


Fig. 7. RDFs of Pd-H and Ag-H systems.

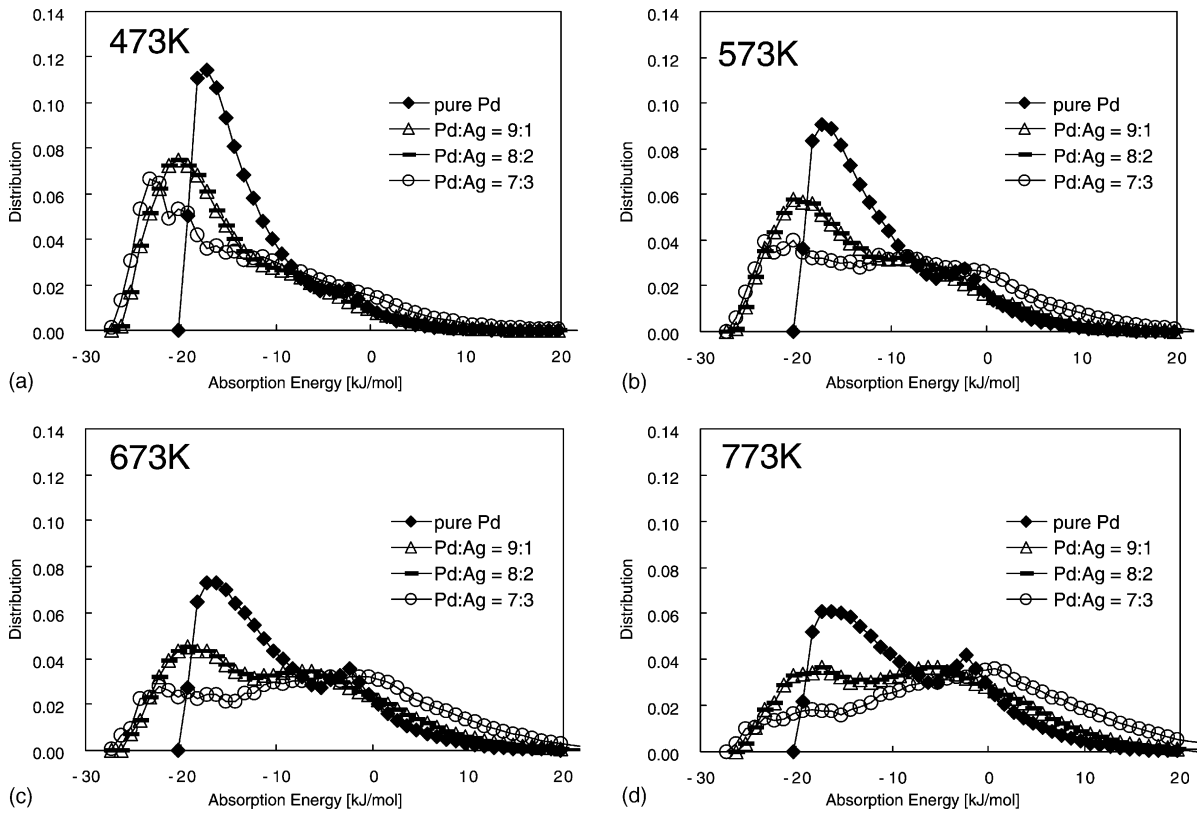


Fig. 8. Absorption energies of hydrogen atoms in Pd-Ag alloys at different temperatures: (a) 473 K; (b) 573 K; (c) 673 K; (d) 773 K.



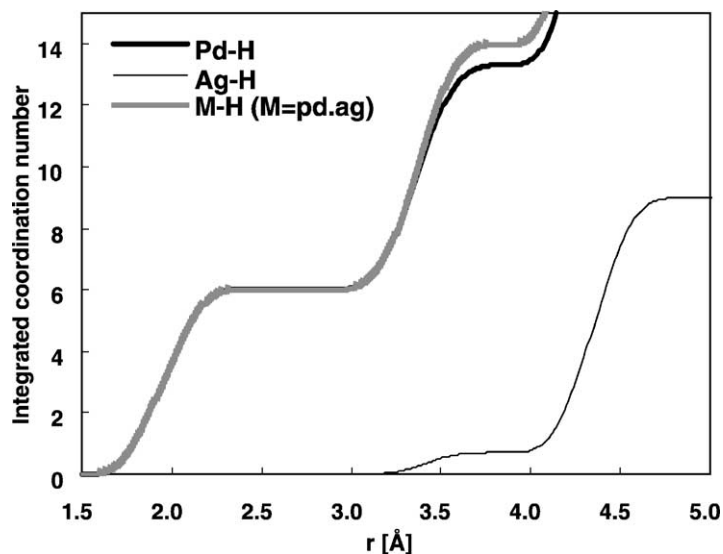


Fig. 9. Integrated coordination number between H and the metal Pd and Ag.

behavior at different sites and hence the energy. On the other hand, for the composition,  $\text{Pd}_{0.7}\text{Ag}_{0.3}$  the peak intensities are reversed at higher temperature, e.g., 773 K. Fig. 9 shows the integrated coordination number of hydrogen atoms absorbed in Pd–Ag alloy. It is clear from this figure that the hydrogen atoms at the lower energy states have six Pd atoms as the first neighbors and seven Pd and one Ag as the second nearest neighbors. Furthermore, it can also be noted that the latter is more stable than the former. This finding on the hydrogen absorption behavior of Pd–Ag is in good agreement with DFT calculations by Løvrvik and Olsen [8].

#### 4. Conclusion

The absorption of hydrogen in Pd and Pd–Ag alloy was investigated using an MC method by considering both the dissociation of hydrogen molecule as well as the subsequent absorption of hydrogen atom in the lattice. We have successfully reproduced the solution enthalpy of hydrogen in pure Pd and Pd–Ag alloy by adjusting the parameters for the interatomic potential. This study also gave the preferable site for hydrogen atom both in Pd in Pd–Ag alloys. Thus, the MC method is very effective to simulate the absorp-

tion behavior of the hydrogen in metals and alloys. Further work is in progress to check the validity of the method for the more complex systems.

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