Pressure-composition isotherms for palladium hydride

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We present Monte Carlo calculations of the pressure-composition isotherms of palladium hydride using recently constructed embedded-atom-method potentials and a Monte Carlo method that allows for volume equilibration as the composition varies.

Metal hydrides are employed in increasing numbers of applications; hydrogen storage for portable power sources, new refrigeration designs, and catalytic converters are just a few of the many uses of hydrogen interacting with metals.[1-6] A property of central importance in some of these applications is the pressure-composition isotherms for the hydride. Palladium hydride is in a class of metal hydrides where the interaction between the metal and the hydrogen results in the system transforming, under increasing hydrogen pressure, from a low concentration phase of hydrogen saturated metal called the α phase, to a high concentration, defective phase of somewhat variable composition called the β phase. For some metals there is a structural phase transformation of the metal lattice in passing from the α to the β phase, but in palladium there is only a change in the lattice constant of the fcc lattice. Palladium hydride may be considered an interstitial alloy, PdH_x, $0 \leq x \leq 1$, where octahedral sites of the fcc metal lattice are occupied by hydrogen.

In this paper we present a Monte Carlo method that we use to generate the pressure-composition isotherms of a model of palladium hydride from a microscopic description of the system. For the microscopic description we use embedded-atom-method (EAM) potentials to represent the interactions. We have previously developed and discussed[7] an improved EAM potential for palladium, which we refer to as PDW3. Using PDW3 for palladium we constructed a companion EAM potential for palladium hydride. Among the additional properties considered in constructing the hydrogen potential was the heat of solution of hydrogen in palladium, the diffusion barrier between the octahedral and tetrahedral sites in the palladium fcc lattice, the expansion of the lattice upon hydrogen loading, and the difference in the binding energy of the hydrogen in vacancies and bulk octahedral sites. The complete potential is defined by an embedding function for each species F_{Pd}, F_H and three pair potentials ϕ_{Pd-Pd}, ϕ_{Pd-H}, and ϕ_{H-H}. In the EAM the potential energy E_{pot} of the system can be written

$$E_{pot} = \sum_{a=1}^{N} F_a(\rho_a) + \sum_{\substack{a,b=1 \\ a<b}}^{N} \phi_{ab}(r_{ab}) , \qquad (1)$$

where ρ_a is the electron density at atom site a due to all other atoms in the system

$$\rho_a = \sum_{\substack{b=1 \\ b \neq a}} \rho_b^{at}(r_{ab}) , \qquad (2)$$

and ρ^{at} is the atomic (at) electron density.

At first it might seem reasonable to try to use the grand canonical ensemble to study the pressure-composition isotherms, however, since the volume is fixed in the grand canonical ensemble, this method is not convenient. There are large volume changes in going from the α to the β phase; the observed change in the lattice constant is around 3.3%. What we would like is a statistical ensemble for which the pressure, temperature, and chemical potential are held fixed. In a constant pressure ensemble the volume will automatically adjust to hold the pressure constant as the composition, or temperature change. For a single species system it is not possible to vary three intensive variables independently because of the Gibbs-Duhem relation which relates them. However, for two (or more) species systems we can derive, rigorously, a statistical ensemble in which T, P, and μ_H and N_{Pd} are held fixed; we call this ensemble the $(TP\mu N)$ ensemble, μ is the chemical potential of hydrogen and the N is the fixed number of palladium atoms. This is a hybrid statistical ensemble which has some properties similar to the single species (TPN) and $(TV\mu)$ ensembles. The $(TP\mu N)$ ensemble describes a system open to hydrogen exchange with a reservoir with chemical potential μ_H, in contact with a thermal reservoir having temperature T and a pressure reservoir having pressure P. This ensemble represents a good way to model experiments where hydrogen gas H_2 at a given temperature, and at various pressures is introduced into a container with the metal sample and one measures the composition for a given pressure. Note that the pressures that are employed in the pressure-composition studies of palladium are on the order of atmospheres and too small to have any measurable effect on the volume; the change in volume of the sample is due to hydrogen absorption or adsorption. The $(TP\mu N)$ ensemble should be useful in a number of applications involving absorption or adsorption where volume or area relaxation is important in attaining equilibrium.

The form of probability distribution for the $(TP\mu N)$ ensemble can be derived, rigorously, by performing three Laplace-Legendre transforms from the microcanonical (EVN_HN_{Pd}) ensemble. The probability that the system with temperature T, pressure P, chemical potential of hydrogen μ_H, and N_{Pd} palladium atoms has volume V, and N_H hydrogen atoms, $W(x,V,N_H)$, where x stands for the positions of all the atoms in the system, is given by

$$W(x,V,N_H)=C(2\pi m_H k_B T)^{3N_H/2}V^N e^{\mu_H N_H/k_B T}$$

$$\times e^{-[E_{pot}(x)+PV]/k_B T}/(h^{3N_H}N_H!) , \quad (3)$$

where C is a constant defined by

$$C=(2\pi m_{Pd}k_B T)^{3N_{Pd}/2}/(h^{3N_{Pd}}N_{Pd}!) . \quad (4)$$

In $(TP\mu N)$ Monte Carlo simulations one carries out four distinct types of trial procedures: (1) the conventional configuration change of the particles; (2) the change of the volume and/or size and shape of the system; (3) a creation event where one attempts to create a particle (hydrogen in our case) at a random position in the system; and (4) a destruction event where one attempts to destroy a particle (hydrogen in our case). In all four cases the acceptance probability can be defined as $P_{accept}=\min(1,W'/W)$, where W' is calculated using Eq. (3) for the trial state and W is calculated using Eq. (3) at the present state.

We arranged a cubic fcc cell with 500 palladium atoms and 1000 "ghost" hydrogen atoms and applied periodic boundary conditions. A ghost variable was assigned to each hydrogen atom; a real particle has the ghost variable as false and a ghost particle has the ghost variable as true. If a hydrogen has the ghost variable equal to true then we call it a ghost particle and do not consider it in calculating the energy. The 1000 ghost particles were initially given random positions inside the computational cell making a grid of 1000 ghost particles spread randomly throughout the system. We also considered a few runs with 2000 ghost particles and obtained the same results. To perform a simulation we specified a pressure (zero), a chemical potential, a temperature, and started the Monte Carlo simulation by performing the four types of Monte Carlo trials and accepting or rejecting the trial moves based on the acceptance probability given by P_{accept}. The amplitude of the configuration trial moves were arranged so that approximately 50% of these moves were accepted, the amplitude of the volume trial moves was arranged so that approximately 50% of these moves were accepted. After each configurational and volume trial we tried to create and then destroy ten particles. One Monte Carlo step represents an attempt to move all the palladium at once, an attempt to move all the real hydrogen at once, an attempt to change the volume, and then ten create and destroy attempts for hydrogens. During each such Monte Carlo step we also move each ghost hydrogen by a small random amount, to help keep the grid of ghost particles randomized over the system. After a real hydrogen is turned into a ghost hydrogen we do not allow it to be turned back into a real hydrogen for at least ten Monte

Carlo steps; this again helps keep the grid of ghost particles randomized over the system. Our general strategy for handling the ghosts was recently used by Ray and Wolf[8] in another ensemble to study the entropy as a function of temperature for liquid palladium modeled by EAM potentials. Such grids of ghost particles have been used before by others in grand canonical ensemble simulations. Carrying out a simulation for a given temperature, chemical potential, and zero pressure the system absorbs or desorbs hydrogen to an equilibrium concentration. The hydrogen atoms are found near the octahedral sites of the palladium lattice, since these are the sites that are the most probable. During the simulation the volume of the system adjusts and follows the hydrogen concentration.

In equilibrium we have equality of the chemical potentials of hydrogen in the two phases corresponding to the reaction $Pd+\frac{1}{2}xH_2\rightleftharpoons PdH_x$

$$\mu_H=\frac{1}{2}\mu_{H_2}=\frac{1}{2}\left[k_B T\ln\left[\frac{P}{P_0(T)}\right]-E_d\right] , \quad (5)$$

where E_d is the heat of dissociation of an H_2 molecule (4.4781 eV), and $P_0(T)$ is given by

$$P_0(T)=(4\pi M k_B T)^{3/2}k_B T 8\pi^2 I_r k_B T/h^5 , \quad (6)$$

with M the mass of the hydrogen atom, I_r the moment of inertia of H_2, and the zero of energy has been taken as the energy of the separated atoms. For a derivation of this result see McQuarrie[9] and the books by the Lässer[5] and Fukai.[6]

In Fig. 1 we show the pressure-composition results determined for our model of palladium hydride at three different temperatures as compared to experimental desorption isotherm data of Frieske and Wicke.[10] The
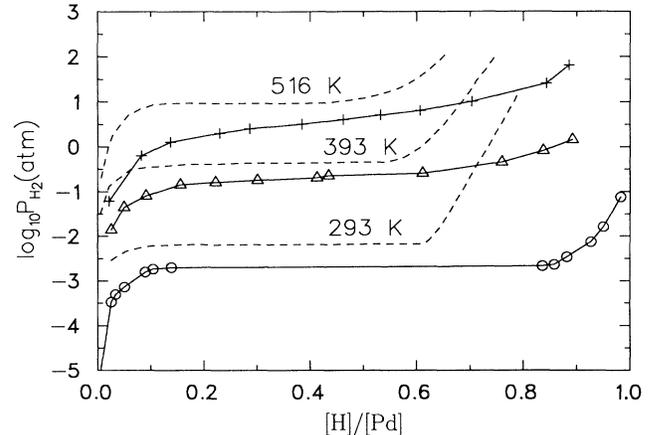
FIG. 1. Pressure-composition isotherms for palladium hydride. The experimental values are from Ref. 10 and are shown by the dashed lines with the temperature labels: 293, 393, and 516 K. The simulation values are given by the solid lines with the circles being for 300 K, the triangles 400 K, and the plus signs 500 K. The pressures are calculated using Eqs. (5) and (6). No zero-point energy corrections have been applied to the simulation values. The lines through the simulation data points are just a guide.

simulation values in Fig. 1 show qualitative agreement with the experimental results including a flatter plateau at lower temperatures and approximately the correct increase of plateau pressure with temperature. The transformation from the α to the β phase is very sharp, that is, a very small change in the chemical potential of hydrogen takes one from the α phase boundary to the β phase boundary. To illustrate this we show in Table I some results from the simulations of hydrogen loading at 300 K. Table I gives the average concentration and average lattice constant, for each chemical potential. These averages were determined in runs of at least 50 000 Monte Carlo moves. Multiple 50 000 move simulations were carried out to confirm convergence and to obtain and error estimates. The uncertainty of the values given in Table I are a few percent or less from this analysis, with the larger errors occurring closer to the phase boundary. Note that a change in the chemical potential from -2.477 to -2.476 eV results in the system changing from the α phase concentration of 0.1385, to the β phase concentration of 0.8362. Although one would expect any adsorption or desorption isotherms to have the same general qualitative appearance as in Figs. 1 and 3, not every potential will have as flat an isotherm as we found for the PDW3 potential. Two other potentials that we studied did not have this behavior, that is, they did not have flat plateaus.[11]

There are also quantitative differences, for example, the maximum concentration for the α phase and the minimum concentration for the β phase are too large in the simulations. We are at present using these results to refine the hydrogen EAM potential. One of the main modifications that we need to make is in the volume change with hydrogen concentration. In Fig. 2 we show the change of the lattice constant with loading at 300 K for PDW3 as compared to the observed change as determined by x-ray diffraction.[12] It is clear from this figure that our lattice expansion is too small.

We are also studying the loading of tritium into palladium using the $(TP\mu N)$ ensemble and EAM potentials. As an example we show in Fig. 3 the 300-K isotherms for tritium loading of palladium as compared to experimental desorption isotherms of Lässer and Klatt;[13] we also

FIG. 2. Lattice constant versus concentration of hydrogen at 300 K as compared to x-ray-diffraction results from Ref. 12. The simulation values are shown by the triangles, while the plus signs denote the experimental values. The lines through the data points are just a guide.

show the hydrogen data at 300 K from Fig. 1 for comparison. Note that in the simulation we obtain the experimentally correct result that $P_T > P_H$ for the same concentration. We have used the same potential to model tritium so the only change is in the probability in Eq. (3), which arises from the mass difference of the two isotopes.

We have presented an ensemble which corresponds to constant temperature, pressure, chemical potential of one species, and particle number of the second species, for a binary system. We have illustrated the method by calculating the pressure-composition isotherms, using an embedded-atom-model potential, for palladium hydride at three temperatures and palladium tritide at one temperature. The calculated results show the same general features as the experimental results with a plateau which is flatter at lower temperature but the concentrations at the α- and β-phase boundaries are too large. We believe

TABLE I. Chemical potential, hydrogen concentration, and lattice constant for hydrogen loading at 300 K. This data is also displayed in Figs. 1, 2, and 3.

μ (eV)	[H]/[Pd]	a (Å)
-2.550	0.0038	3.9037
-2.500	0.0256	3.9075
-2.495	0.0333	3.9094
-2.490	0.0502	3.9124
-2.480	0.0894	3.9193
-2.478	0.1041	3.9221
-2.477	0.1385	3.9278
-2.476	0.8362	4.0332
-2.475	0.8584	4.0361
-2.460	0.9267	4.0449
-2.450	0.9500	4.0485
-2.430	0.9825	4.0520
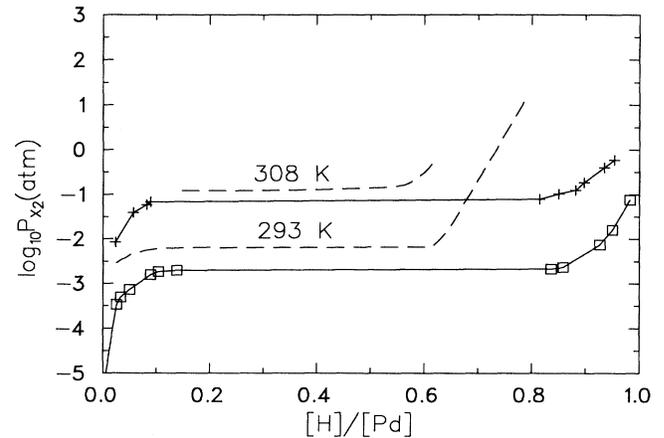
FIG. 3. Pressure-composition isotherms at 300 K for tritium and hydrogen. The experimental data are shown by the dashed lines with the tritium data from Ref. 13 being the 308-K data and the hydrogen at 293 K is the same experimental data as in Fig. 1. The simulation data for tritium is the solid line with the plus signs, while the hydrogen data is the solid line with the squares; both at 300 K.

a main defect of the potential is the volume expansion versus hydrogen/tritium concentration and in our next refinement of the potential we shall make this property more accurate.

We have compared our simulations with the experimental desorption isotherms of hydrogen and tritium in palladium; these are the results most often published, since the desorption experiments are more reproducible. Although absorption and adsorption coincide in the α and β phase, respectively, there is hysteresis between absorption and desorption in the mixed phase plateau region. We are exploring whether our model predicts this hysteresis in the plateau region of the phase diagram, our simulation results presented are for absorption.

Because of the large zero-point energy of hydrogen, our simulations should contain a correction for the zero-point energy of hydrogen. If ε_0 is average zero-point energy per hydrogen atom then $E_{tot} = E_{pot} + N_H \varepsilon_0$, replaces E_{pot} in Eq. (3). Using this in Eq. (3) and defining

$\mu_H(sim) = \mu_H - \varepsilon_0$, we see that the only effect of this substitution is that the true chemical potential μ_H must be obtained by adding the zero-point energy ε_0 to the value of the chemical potential determined in the simulation μ_H (sim). In Figs. 1 and 3 this correction would shift the simulation curves up by a pressure increment corresponding to the average zero-point energy correction. One problem with this type of correction in this work, is that the zero-point energy changes by a significant amount with hydrogen concentration. In the present stage of our study we have not included a zero-point energy correction. Note that for tritium the zero-point energy correction would be reduced by $(1/3)^{1/2}$ so we would expect the tritium results to compare better with experiment, and Fig. 3 shows that this is indeed the case.

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