

# SANDIA REPORT

SAND2011-2340  
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Printed April, 2011

## Diffusional exchange of isotopes in a metal hydride sphere

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## Abstract

This report describes the Spherical Particle Exchange Model (SPEM), which simulates exchange of one hydrogen isotope by another hydrogen isotope in a spherical metal hydride particle. This is one of the fundamental physical processes during isotope exchange in a bed of spherical metal particles and is thus one of the key components in any comprehensive physics-based model of exchange. There are two important physical processes in the model. One is the entropy of mixing between the two isotopes; the entropy of mixing is increased by having both isotopes randomly placed at interstitial sites on the lattice and thus impedes the exchange process. The other physical process is the elastic interaction between isotope atoms on the lattice. The elastic interaction is the cause for  $\beta$ -phase formation and is independent of the isotope species.

In this report the coupled diffusion equations for two isotopes in the  $\beta$ -phase hydride are solved. A key concept is that the diffusion of one isotope depends not only on its concentration gradient, but also on the concentration gradient of the other isotope. Diffusion rate constants and the chemical potentials for deuterium and hydrogen in the  $\beta$ -phase hydride are reviewed because these quantities are essential for an accurate model of the diffusion process. Finally, a summary of some of the predictions from the SPEM model are provided.

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## Introduction

Here, the Spherical Particle Exchange Model (SPEM) is described. The SPEM code simulates exchange of one hydrogen isotope for another hydrogen isotope in a spherical metal or metal hydride particle. This is one of the fundamental physical processes during isotope exchange in a bed of spherical metal particles and is thus one of the key components in a comprehensive physics-based model of exchange.

There have been a number of models created for hydrogen exchange in a bed, but none of them treat the exchange process in the metal particles with the fidelity of this model [1-9]. In the SPEM model, the interaction between the two isotopes in the interstitial sites of the metal hydride is described with a fundamental physical model rather than with phenomenological parameters. The SPEM model includes the important fact that diffusion of one isotope (say hydrogen) depends not only on the concentration gradient of hydrogen, but also on the concentration gradient of deuterium. Thus for example the diffusion equations can be written:

$$\begin{aligned}j_H &= -D_{HH}\nabla c_H - D_{HD}\nabla c_D, \\j_D &= -D_{DD}\nabla c_D - D_{DH}\nabla c_H,\end{aligned}\tag{1}$$

where  $j_K$  (mol/cm<sup>2</sup>·s) is the flux of isotope  $K$ ,  $\tilde{\nabla}c_K$  (mol/cm<sup>4</sup>) is the concentration gradient, and the diffusion rates,  $D_{KK'}$  (cm<sup>2</sup>/s), include cross-terms [10]. SPEM solves this coupled diffusion equation subject to a boundary condition of the concentrations of the two isotopes in the near-surface region. Here, slightly smoothed step functions are generally supplied for the boundary condition to avoid discontinuities. However, in a unified model of exchange, the boundary conditions would be coupled to models of gas flow, surface adsorption, and uptake of surface species in the near-surface region.

In writing this report there are two primary goals: One is to derive the equations and detail the physical processes involved in the model; the other is to document the sources of experimentally known quantities, especially diffusion rates and chemical potentials of hydrogen isotopes in beta-phase palladium hydride ( $\beta$ -Pd) that are required as input to the model. A final goal is to identify conditions under which the exchange of isotopes by bulk diffusion in palladium may be a rate-limiting process in a working exchange bed and to examine the “isotope effect” when hydrogen evolution (not exchange) by deuterium (H→D) could be faster than deuterium evolution by hydrogen (D→H).

Consider the interdiffusion of two species on a lattice; this provides the framework for the following sections that review the experimental data upon which SPEM is based.

## Interdiffusion of Two Species on a Lattice

To generalize from the well-known case of a single species diffusing to the case of two or more interdiffusing species, the discussion is formulated in terms of the chemical potential and

mobility for each species. For a single diffusing species at moderate concentrations, the diffusion flux of hydrogen can be written in two different ways:

$$j_{\text{H}} = -M_{\text{H}}c_{\text{H}}\nabla\mu_{\text{H}} = -D_{\text{H}}^{\text{Fick}}\nabla c_{\text{H}}. \quad (2)$$

where  $\mu_{\text{H}}$  (erg/mol) is the chemical potential of hydrogen, and  $M_{\text{H}}$  (mol·s/g or mol·cm<sup>2</sup>/erg·s) is the mobility of hydrogen. Equation (2) defines the mobility for hydrogen as:

$$M_{\text{H}} = \frac{D_{\text{H}}^{\text{Fick}}}{c_{\text{H}}} \left( \frac{\partial\mu_{\text{H}}}{\partial c_{\text{H}}} \right)^{-1} = D_{\text{H}}^{\text{Fick}} \left( \frac{\partial\mu_{\text{H}}}{\partial \ln c_{\text{H}}} \right)^{-1}. \quad (3)$$

A closely related concept is the dimensionless thermodynamic factor,  $\gamma$ , defined as the derivative of the activity of hydrogen in palladium:

$$\gamma = \frac{\partial \ln a_{\text{H(Pd)}}}{\partial \ln c_{\text{H}}}, \quad (4)$$

where the dimensionless activity is:

$$\ln a_{\text{H}} = \frac{\mu_{\text{H}}(c_{\text{H}}, T)}{RT} - \frac{\mu_{\text{H}}^0(T)}{RT}, \quad (5)$$

and  $\mu_{\text{H}}^0$  is the chemical potential of a reference state,  $R$  (erg/mol·K) is the gas constant, and  $T$  (K) is temperature.

Substituting (5) into (4) yields:

$$\frac{\partial\mu_{\text{H}}}{\partial \ln c_{\text{H}}} = \gamma RT, \quad (6)$$

and substituting the preceding equation into (3) specifies that

$$M_{\text{H}} = \frac{D_{\text{H}}^{\text{Fick}}}{\gamma RT}. \quad (7)$$

The Einstein diffusion rate is a concentration independent diffusion rate (e.g., used to describe self diffusion) related to the Fickian diffusion rate by

$$D_{\text{H}}^{\text{Fick}} = \gamma D_{\text{H}}^{\text{Ein}}. \quad (8)$$

The Einstein diffusion rate obeys an Arrhenius law and may be written as:

$$D_{\text{H}}^{\text{Ein}} = D_{0,\text{H}} \exp\left(-\frac{E_{0,\text{H}}}{RT}\right). \quad (9)$$

Finally, at higher concentration in  $\beta$ -Pd, site-blocking becomes increasingly important as the number of vacancies in the lattice becomes small. Site blocking reduces the overall diffusion rate, but does not affect the Einstein diffusion rate or the mobility. The Fickian diffusion rate at high concentrations is:

$$D_{\text{H}}^{\text{Fick}^*} = c_{\text{V}} D_{\text{H}}^{\text{Fick}} = c_{\text{V}} \gamma D_{\text{H}}^{\text{Ein}}. \quad (10)$$

For high concentrations and a single diffusing species, Fick's law becomes:

$$j_{\text{H}} = -D_{\text{H}}^{\text{Fick}^*} \nabla c_{\text{H}} = -c_{\text{V}} D_{\text{H}}^{\text{Fick}} \nabla c_{\text{H}} = -c_{\text{V}} \gamma D_{\text{H}}^{\text{Ein}} \nabla c_{\text{H}}. \quad (11)$$

The alternative formulation in terms of chemical potentials is:

$$j_{\text{H}} = -c_{\text{V}} c_{\text{H}} M_{\text{H}} \nabla \mu_{\text{H}}. \quad (12)$$

The preceding equation is adopted because it is readily adapted to the case of two isotopes. For two isotopes, the concentration of vacancies is replaced by  $c_{\text{V}} = (1 - c_{\text{H}} - c_{\text{D}})$ . The mobility term is unchanged.

For two interdiffusing species, the important point is that the chemical potential of H depends not only on the concentration of H, but also on the concentration of D. The chemical potential is  $\mu_{\text{H}}(c_{\text{H}}, c_{\text{D}})$  and the diffusion equations for the two isotopes become coupled:

$$\begin{aligned} j_{\text{H}} &= -(1 - c_{\text{H}} - c_{\text{D}}) c_{\text{H}} M_{\text{H}} \left( \frac{\partial \mu_{\text{H}}}{\partial c_{\text{H}}} \nabla c_{\text{H}} + \frac{\partial \mu_{\text{H}}}{\partial c_{\text{D}}} \nabla c_{\text{D}} \right), \\ j_{\text{D}} &= -(1 - c_{\text{H}} - c_{\text{D}}) c_{\text{D}} M_{\text{D}} \left( \frac{\partial \mu_{\text{D}}}{\partial c_{\text{H}}} \nabla c_{\text{H}} + \frac{\partial \mu_{\text{D}}}{\partial c_{\text{D}}} \nabla c_{\text{D}} \right). \end{aligned} \quad (13)$$

Next, the experimental estimation of the chemical potentials and the mobilities for hydrogen and deuterium in the  $\beta$ -Pd are described.

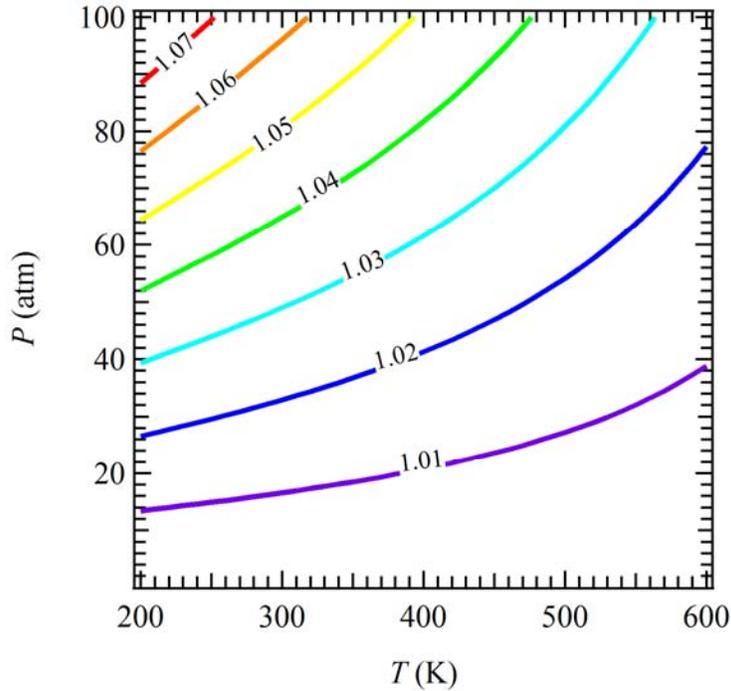
## Chemical Potentials of Hydrogen and Deuterium

### Fugacity of Hydrogen Gas

At high pressures and at low temperatures, hydrogen, deuterium and tritium depart from the ideal gas law. This behavior is not a direct component in this model, however it is important when estimating chemical potentials and mobilities, which are inputs to SPEM. The ranges of pressure and temperature where non-ideal gas behavior becomes significant are identified. For such pressures and temperatures, the activities of hydrogen and deuterium will no longer equal the

partial pressures of the gases. This would affect the boundary conditions for the SPEM model if it this behavior is incorporated into a multi-physics simulation of a system at high pressures and low temperature.

Because the SPEM model is concerned only with solid-state diffusion, fugacity enters only indirectly. However, state-of-the-art measurements of diffusion rates and of pressure, composition, and temperature (PCT) curves generally include pressures and temperatures for which hydrogen isotopes depart from ideal gas behaviors. To reach high stoichiometries, for PdH, high pressures must be applied and under these conditions the gas-phase equation of state deviates significantly from the ideal gas law. The conditions for which fugacity is not equal to pressure and in which non-ideal gas behavior must be included in a physical model of exchange are identified. Figure 1 summarizes the range of pressure and temperature for which non-ideal gas behavior must be incorporated in the exchange process.



**Figure 1: Fugacity non-ideality,  $f(P,T)/P$ , as a function of pressure and temperature.**

Fisher [11] defined the range of temperatures and pressures for which non-ideal gas behavior becomes important by fitting compressibility with a virial expansion. For a mole of an ideal gas,  $PV = RT$ ; however, for a real gas  $PV = ZRT$  where  $Z$  is the dimensionless compressibility, which is estimated using a series expansion:

$$Z(P,T) = 1 + B_p(T) \frac{P}{T} + C_p(T) \left(\frac{P}{T}\right)^2 + D_p(T) \left(\frac{P}{T}\right)^3 + E_p(T) \left(\frac{P}{T}\right)^4 + \dots \quad (14)$$

Fugacity is computed as:

$$\ln \left[ \frac{f(P, T)}{P} \right] = B_p \frac{P}{T} + \frac{1}{2} C_p \left( \frac{P}{T} \right)^2 + \frac{1}{3} D_p \left( \frac{P}{T} \right)^3 + \frac{1}{4} E_p \left( \frac{P}{T} \right)^4 + \dots \quad (15)$$

A contour plot of the fugacity of hydrogen as a function of pressure and temperature is shown in Figure 1. The contours indicate the degree to which the range of pressures and temperatures yield non-ideal behavior.

### **Chemical Potential of Mixing**

Other inputs required for SPEM are the chemical potentials for H and D in Pd, which are composed of two contributors: that due to mixing, and that from elastic and electronic interactions. Recall that three species are considered on the lattice, hydrogen, deuterium, and vacancies. Denote the total number of hydrogen atoms occupying sites as  $N_H$ , with the numbers of deuterium atoms and vacancies being  $N_D$  and  $N_V$ , respectively. The total number of sites is  $N = N_H + N_D + N_V$ . Boltzmann's equation gives the entropy of mixing as [12]:

$$\Delta S_m = k_B \ln(\Omega), \quad (16)$$

where  $\Omega$  is the total number of atomics permutations corrected for the fact that hydrogen atoms are indistinguishable (and likewise for  $N_D$  and  $N_V$ ):

$$\Omega = \frac{N!}{N_H! N_D! N_V!}. \quad (17)$$

Applying Stirling's approximation,  $\ln(n!) \approx n \ln(n) - n - 1$ , results in:

$$\begin{aligned} \Delta S_m &= -k_B \left[ N_H \ln \left( \frac{N_H}{N} \right) + N_D \ln \left( \frac{N_D}{N} \right) + N_V \ln \left( \frac{N_V}{N} \right) \right], \\ &= -nR \left[ c_H \ln(c_H) + c_D \ln(c_D) + c_V \ln(c_V) \right]. \end{aligned} \quad (18)$$

The gas constant is equal to Boltzmann's constant,  $k_B$  (erg/K), times Avogadro's number and  $n_H$ ,  $n_D$  and  $n_V$  are the number of moles of hydrogen, deuterium, and vacancies. The total number of moles of lattice sites is  $n = n_H + n_D + n_V$ .

The Gibbs free energy of mixing is:

$$\Delta G_m = nRT \left[ c_H \ln(c_H) + c_D \ln(c_D) + (1 - c_H - c_D) \ln(1 - c_H - c_D) \right]. \quad (19)$$

The mixing components of the chemical potential for the isotopes are obtained by differentiating the Gibbs free energy with respect to isotope concentration:

$$\begin{aligned}\mu_{\text{H}}^{\text{mix}} &= RT \left[ \ln(c_{\text{H}}) - \ln(1 - c_{\text{H}} - c_{\text{D}}) \right], \\ \mu_{\text{D}}^{\text{mix}} &= RT \left[ \ln(c_{\text{D}}) - \ln(1 - c_{\text{H}} - c_{\text{D}}) \right].\end{aligned}\quad (20)$$

The mobilities are defined in terms of partial derivative of the chemical potential with respect to concentrations as in (12) above. The following partial derivatives result:

$$\begin{aligned}\frac{\partial \mu_{\text{H}}^{\text{mix}}}{\partial c_{\text{H}}} &= RT \left( \frac{1}{c_{\text{V}}} + \frac{1}{c_{\text{H}}} \right), \\ \frac{\partial \mu_{\text{H}}^{\text{mix}}}{\partial c_{\text{D}}} &= \frac{\partial \mu_{\text{D}}^{\text{mix}}}{\partial c_{\text{H}}} = RT \left( \frac{1}{c_{\text{V}}} \right), \\ \frac{\partial \mu_{\text{D}}^{\text{mix}}}{\partial c_{\text{D}}} &= RT \left( \frac{1}{c_{\text{V}}} + \frac{1}{c_{\text{D}}} \right).\end{aligned}\quad (21)$$

### **Chemical Potential due to Elastic and Electronic Interactions**

The second factor affecting the chemical potential of hydrogen isotopes in Pd is the excess chemical potential due to electronic and elastic effects. The quantity of interest is the excess chemical potential for hydrogen in  $\beta$ -Pd (or deuterium in palladium deuteride), which can be obtained from PCT measurements [11, 13].

Wolfer et al. [14] present a detailed analysis based on the work of Lässer and Powell [15]. For  $\beta$ -PdH, the chemical potential for hydrogen isotopes in the metal is:

$$\mu_{\text{H}}(c_{\text{H}}, T) = \bar{G}_{\text{H}}^{\infty}(T) + RT \ln \left( \frac{c_{\text{H}}}{1 - c_{\text{H}}} \right) + \mu_{\text{H}}^{\text{ee}}(c_{\text{H}}, T). \quad (22)$$

The partial Gibbs free energy at infinite dilution,  $\bar{G}_{\text{H}}^{\infty}(T)$  (erg/mol), is known from experimental work measuring PCT curves in the dilute  $\alpha$ -Pd. Lässer and Powell [15] provide an analytical fit for this quantity. Because only the composition derivative of the chemical potential is needed for SPEM,  $\bar{G}_{\text{H}}^{\infty}(T)$  is not discussed further. The second term in (22) is the mixing contribution to the chemical potential for mixing of hydrogen atoms and vacancies at interstitial sites. The remaining term, the excess chemical potential, is obtained by fitting to PCT data. Wolfer et al. [15] present a plot of this quantity in erg/mol, which depends linearly on stoichiometry:

$$\mu_{\text{H}}^{\text{ee}}(c_{\text{H}}, T) = -1.595 \times 10^{12} + 1.772 \times 10^{12} c_{\text{H}}. \quad (23)$$

They also concluded that the excess chemical potential is independent of both temperature and isotope. Thus, (23) is applicable to hydrogen, deuterium, and tritium. Based on this result, we assume that the elastic and electronic interactions are also independent of isotope, thus

$$\mu_{\text{H}}^{\text{ee}}(c_{\text{H}}, c_{\text{D}}, T) = \mu_{\text{D}}^{\text{ee}}(c_{\text{H}}, c_{\text{D}}, T) = -1.595 \times 10^{12} + 1.772 \times 10^{12} (c_{\text{H}} + c_{\text{D}}). \quad (24)$$

It is also important to verify that this expression is in agreement with earlier investigations. Majorowski and Baranowski [16] give a value for  $\ln a_{\text{H}(\text{Pd})}$  based on the work of Tkacz and Baranowski [17] and Wicke and Nernst [13]:

$$\ln a_{\text{H}(\text{Pd})} = \frac{\ln a_{\text{H}_2}}{2} = -\frac{2.1 \times 10^{12} - 1.886 \times 10^{12} c_{\text{H}}}{RT} + \frac{2.227 \times 10^9}{R} + \ln \left( \frac{c_{\text{H}}}{1 - c_{\text{H}}} \right). \quad (25)$$

Because the definition of chemical potential is  $m_{\text{H}} = m_{\text{H}}^0 + RT \ln a_{\text{H}}$ , the relevant derivative is

$$\frac{d\mu_{\text{H}}}{dc_{\text{H}}} = 1.886 \times 10^{12} + \frac{RT}{1 - c_{\text{H}}}. \quad (26)$$

The first term is from the excess chemical potential, the second represents the entropy of mixing. The agreement with Wolfer et al. [13] is within experimental error. Majorowski and Baranowski [14] comment on the fact that (26) also holds for deuterium in agreement with the findings of Wolfer et al. [16] that it is isotope independent. Using (6), (26) yields the following value for the thermodynamic constant of hydrogen:

$$\gamma = \frac{1.886 \times 10^{12} c_{\text{H}}}{RT} + \frac{1}{1 - c_{\text{H}}}. \quad (27)$$

## Diffusion Rates for Single Isotopes in $\beta$ -phase Pd Hydride

Finally, to quantify diffusion rates in  $\beta$ -Pd, the measured  $D_{\text{H}}^{\text{Fick}^*}$  (cm<sup>2</sup>/s) of Majorowski and Baranowski [16] are used. Using (8), (9), (10), and (26), the Fickian diffusion constant (with site blocking) is written as:

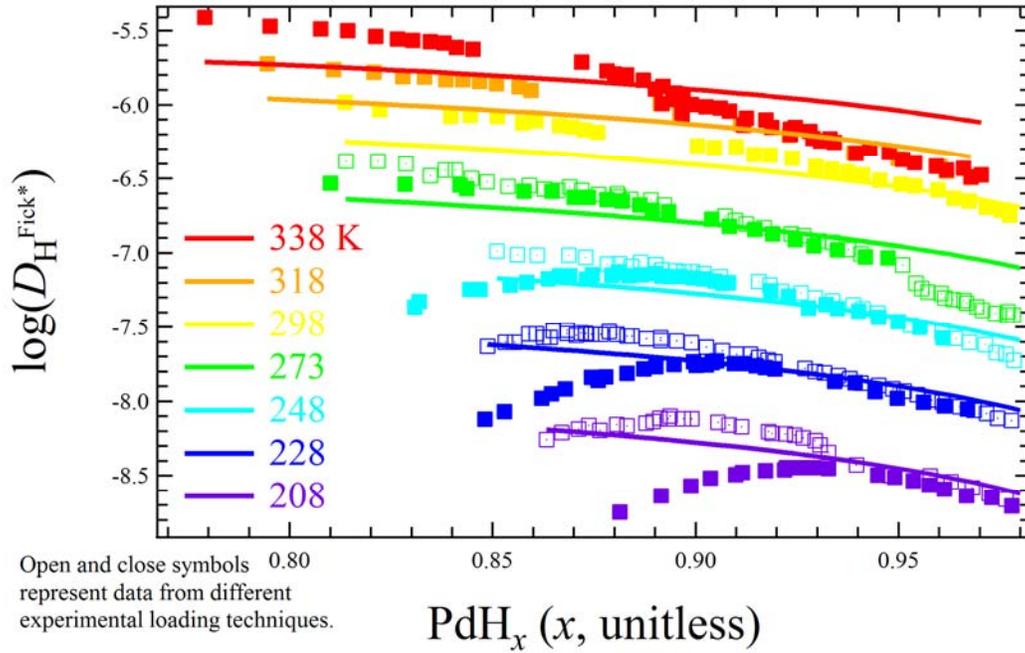
$$D_{\text{H}}^{\text{Fick}^*} = c_{\text{V}} \gamma D_{\text{H}}^{\text{Ein}} = (1 - c_{\text{H}}) \left( \frac{1.886 \times 10^{12} c_{\text{H}}}{RT} + \frac{1}{1 - c_{\text{H}}} \right) D_{0,\text{H}} \exp \left( -\frac{E_{0,\text{H}}}{RT} \right). \quad (28)$$

Unknown parameters  $D_{0,\text{H}}$  (cm<sup>2</sup>/s) and  $E_{0,\text{H}}$  (erg/mol), were fit to the log data (to apply suitable weighting to the errors) of Majorowski and Baranowski [16, Figures 1 and 3]. Table 1 lists the best-fit values. Figure 2 plots the digitized data along with the fitted rates from (28). The reader will notice that measured diffusion rates actually decrease for lower stoichiometry and temperature. This observation is not well understood by the original authors or by the present authors. Equation (28) is identical to the equations used by Majorowski and Baranowski [16, Eqns. 12, 13, 15, and 16] to analyze their data. It would, of course, be possible to simply fit the data with an arbitrary curve, but it would then not be possible to extend the model to the case of mixed isotope diffusion and the equation would lose its physics-based meaning. Note that the maximum error in the fitted diffusion rates is approximately a factor of  $\sqrt{10}$ , which is roughly

equivalent to how the diffusion rate changes with a 20-K change in temperature. Although such temperature changes are possible in actual exchange reactions, this physics-based fit should provide acceptable results in a multiphysics simulation.

**Table 1: Best-fit diffusivities and activation energies for H and D. These fitting parameters should only be used with (28) to obtain Fickian diffusion rates.**

Isotope	$D_0$ (cm <sup>2</sup> /s)	$E_0$ (erg/mol)
H	$5.470 \times 10^{-3}$	$2.604 \times 10^{11}$
D	$2.103 \times 10^{-2}$	$2.818 \times 10^{11}$



**Figure 2: Data and fit for hydrogen diffusing into  $\beta$ -Pd [16, Eqns. 12, 13, 15, and 16].**

## Calculation Coupled Diffusion Rates

There is now sufficient information to calculate the coupled diffusion rates  $D_{HH}(c_H, c_D)$ ,  $D_{DD}(c_H, c_D)$ , and  $D_{HD}(c_H, c_D) = D_{DH}(c_H, c_D)$  in (1). Substituting the definition of  $M_H$  from (7) into (8) and then into (9) yields the mobility of hydrogen as:

$$M_H = \frac{D_{0,H}}{RT} \exp\left(\frac{E_{0,H}}{RT}\right). \quad (29)$$

Now, the partial diffusion rates found in (1) can be calculated. Equating (1) and (13) produces:

$$\begin{aligned}
D_{\text{HH}} &= c_{\text{V}}c_{\text{H}}D_{\text{H}}^{\text{Ein}} \left( \frac{\partial \mu_{\text{H}}^{\text{mix}}}{\partial c_{\text{H}}} + \frac{\partial \mu_{\text{H}}^{\text{ee}}}{\partial c_{\text{H}}} \right), & D_{\text{HD}} &= c_{\text{V}}c_{\text{H}}D_{\text{H}}^{\text{Ein}} \left( \frac{\partial \mu_{\text{H}}^{\text{mix}}}{\partial c_{\text{D}}} + \frac{\partial \mu_{\text{H}}^{\text{ee}}}{\partial c_{\text{D}}} \right), \\
D_{\text{DH}} &= c_{\text{V}}c_{\text{D}}D_{\text{D}}^{\text{Ein}} \left( \frac{\partial \mu_{\text{D}}^{\text{mix}}}{\partial c_{\text{H}}} + \frac{\partial \mu_{\text{D}}^{\text{ee}}}{\partial c_{\text{H}}} \right), & D_{\text{DD}} &= c_{\text{V}}c_{\text{D}}D_{\text{D}}^{\text{Ein}} \left( \frac{\partial \mu_{\text{D}}^{\text{mix}}}{\partial c_{\text{D}}} + \frac{\partial \mu_{\text{D}}^{\text{ee}}}{\partial c_{\text{D}}} \right).
\end{aligned} \tag{30}$$

In the preceding equations, the following values for the various terms are: concentration of vacancies is  $c_{\text{V}} = 1 - c_{\text{H}} - c_{\text{D}}$ ; the Einstein diffusion rates are from the Arrhenius equation (9) with fitting parameters given in Table 1; the partial derivatives of the mixing chemical potentials are given by (21); and the partial derivatives of the excess chemical potential are given by (24).

## Diffusion in Spherical Coordinates

SPEM assumes rotational symmetry of a spherical particle so that the concentration of the isotope is a function only of the radial distance from the center ( $r = 0$ ). The model calculates two transient concentration profiles,  $c_{\text{H}}(r, t)$  and  $c_{\text{D}}(r, t)$ . Of course, initial conditions are required i.e.,  $c_{\text{H}}(r, t = 0)$  and  $c_{\text{D}}(r, t = 0)$ . One boundary condition is the concentration of the isotopes in the near-surface region as a function of time,  $c_{\text{H}}(r = r_0, t)$  and  $c_{\text{D}}(r = r_0, t)$ . Here  $r_0$  is the radius of the particle. The other boundary condition is zero flux at the sphere's center,  $\partial c(r = 0, t) / \partial r = 0$ . For a complete multi-physics simulation of a working exchange bed, the interaction between the gas phase and the bulk would be incorporated by coupling the near-surface concentrations or the surface flux using a surface model for adsorption and uptake.

In spherical coordinates the standard diffusion equation for a single isotope is:

$$\frac{\partial c_{\text{H}}}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( Dr^2 \frac{\partial c_{\text{H}}}{\partial r} \right), \tag{31}$$

where the Fickian diffusion rate,  $D$ , is a function of  $c_{\text{H}}$  and temperature. For two diffusing species, the coupled diffusion equations become:

$$\begin{aligned}
\frac{\partial c_{\text{H}}}{\partial t} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( D_{\text{HH}} \frac{\partial c_{\text{H}}}{\partial r} + D_{\text{HD}} \frac{\partial c_{\text{D}}}{\partial r} \right) \right], \\
\frac{\partial c_{\text{D}}}{\partial t} &= \frac{1}{r^2} \frac{\partial}{\partial r} \left[ r^2 \left( D_{\text{DD}} \frac{\partial c_{\text{D}}}{\partial r} + D_{\text{DH}} \frac{\partial c_{\text{H}}}{\partial r} \right) \right].
\end{aligned} \tag{32}$$

These coupled equations are solved numerically (subject to appropriate boundary and initial conditions) using a predictor-corrector method. The FORTRAN code for solution of this set of differential equations is given in Appendix A. Alternately, they could be solved using Mathematica or any other packaged program for solution of partial differential equations. Recall that the diffusion constants depend on both  $c_{\text{H}}$  and  $c_{\text{D}}$ .

# SPEM Modeling of Isotope Effects in Exchange

## Boundary and Initial Conditions

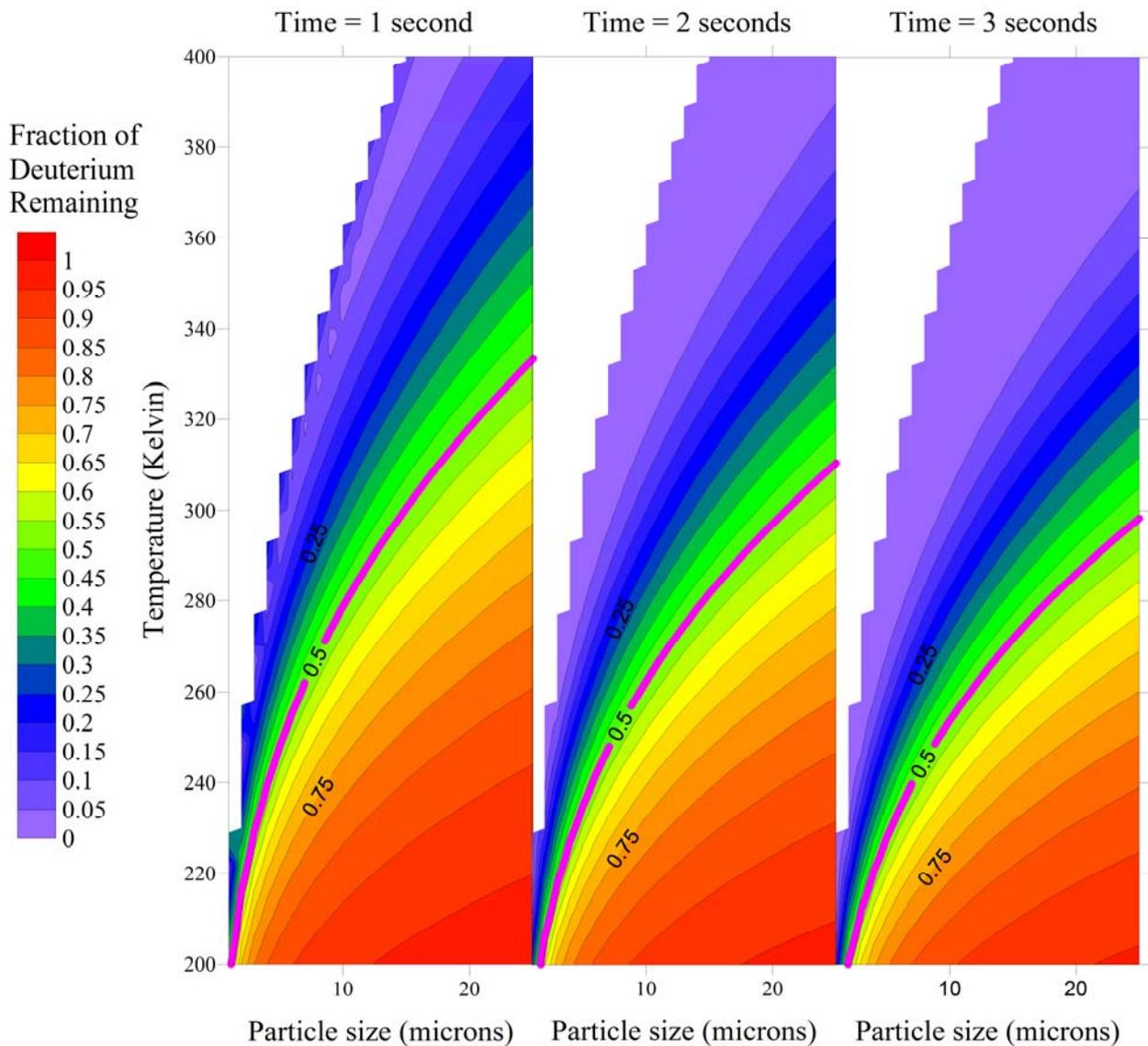
To use the SPEM code, the initial isotope loading of the spherical hydride particle must be specified. To avoid numerical problems, isotope loadings must not be set to zero; instead use a small positive concentration (e.g., 0.001). Typical initial loadings are PdD<sub>0.649</sub> and PdH<sub>0.001</sub> although Santandrea and Behrens [18] provide the details on how to calculate H and D loadings in Pd as a function of pressure and temperature. These starting concentrations are uniform (independent of the radial position,  $r$ ). At  $t = 0$ , the near surface concentrations are changed to PdD<sub>0.001</sub> and PdH<sub>0.699</sub> and held constant (this assumes that the surface kinetics are instantaneous and that the hydrogen goes to its equilibrium concentration in  $\beta$ -Pd hydride at 298 K and 689,475 barye (10 psi). Similarly, PdD<sub>0.649</sub> corresponds to the equilibrium concentration of deuterium in  $\beta$ -Pd deuteride at 298 K and 689,475 barye.

When solving partial differential equations numerically, it is good practice to avoid instantaneous changes in concentration boundary conditions. In reality, instantaneous changes in concentrations are not possible in a physical experiment: computationally they lead to numerical instabilities, particularly for large time steps. To avoid problems with the numerical solution, we sometimes used a linear ramp in concentration vs. time boundary condition. In all cases for which a linear ramp was used, the ramp time was several orders of magnitude shorter than the exchange time.

Another issue in any finite element numerical solution is selection of an appropriate time step. If the time step is too large, numerical instabilities result. If the time step is too small, the problem can be computationally burdensome. Because diffusion rates are an exponential function of temperature, small changes in temperature often produce large changes in the optimum time step. An appropriate time step is selected based on the following simple calculation. Solving the characteristic diffusion length [19] for time yields  $t = L^2/4D$  where  $L$  (cm) is the characteristic length equal to the finite difference cell size and  $D$  (cm<sup>2</sup>/s) is the diffusion rate. The maximum time step for the model should be no more than  $t/10$ .

## Predicting Exchange Rates as a Function of Temperature and Particle Size

One important question that the SPEM code can resolve is whether, for a given exchange time and temperature, when is bulk diffusion in  $\beta$ -Pd likely to be a rate limiting step? Figure 3 shows contour plots of deuterium remaining in a spherical particle during D $\rightarrow$ H exchange. The three contour plots corresponding to one, two, and three seconds of total exchange time. The particle size ( $x$ -axis) is from 1 to 25  $\mu\text{m}$ . The temperature ( $y$ -axis) ranges from 200 to 400 K. The contour corresponding to 50% exchange is highlighted in pink and labeled "0.5." The bulk diffusion is likely to be rate limiting for large particle sizes and/or low temperatures.



**Figure 3: Contour plots of the fraction of deuterium remaining during a D→H exchange after 1, 2, and 3 seconds. The white space is where full exchange was essentially completed and the code was not asked to make calculations there.**

### **Calculations for Analysis**

One of the challenges in modeling exchange is to understand the “isotope effect.” This refers to the experimental observation that D→H exchanges are faster than H→D exchanges. In other words, the evolution of hydrogen from a bed loaded with hydrogen and dosed with deuterium is faster than the evolution of deuterium from a bed dosed by hydrogen [5]. The purpose of this study was to determine whether the simulated exchange process in a single spherical Pd particle could produce the observed effect. In this study, the two relevant inputs to SPEM are systematically manipulated to determine their effect on exchange.

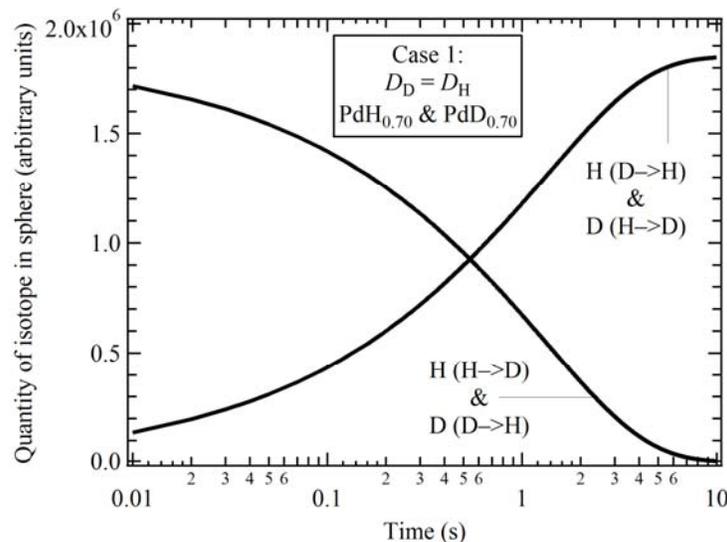
Within the framework of the SPEM code there are two isotope-dependent input variables. The first is the difference in the bulk diffusion rates of the two isotopes, hydrogen in  $\beta$ -Pd hydride, and deuterium in  $\beta$ -Pd deuteride. The Einstein diffusion constant data of Majorowski and Baranowski [16, Fig. 10] suggests that diffusion of deuterium is about 1.7 times faster than the diffusion of hydrogen at temperatures near room temperature (see also Figure 2).

The other isotope-dependent variable is the solubility (or stoichiometry) of each isotope in the hydride at the relevant operating pressure of the device. The difference in solubility of the two isotopes (at the same overpressure) is illustrated by Figure 1 of Wolfer et al. [14]. For pressures less than about 68,947,573 barye (1,000 psi), the solubility of hydrogen is about 5% larger than the solubility of deuterium.

To understand the role of these two variables, the eight simulations listed in Table 2 were conducted. Each cell in the table represents two exchanges, H $\rightarrow$ D and D $\rightarrow$ H. Case 1 is a trivial case in which both the diffusion rates and the stoichiometries of the two isotopes are identical. This verified that, with identical inputs for H and D, H $\rightarrow$ D and D $\rightarrow$ H runs are identical. This also provided a simple reference case for quantitative comparison to the other cases. Figure 4 shows the total quantities of hydrogen and deuterium present in a 10- $\mu$ m sphere at 300 K during the Case-1 exchange event.

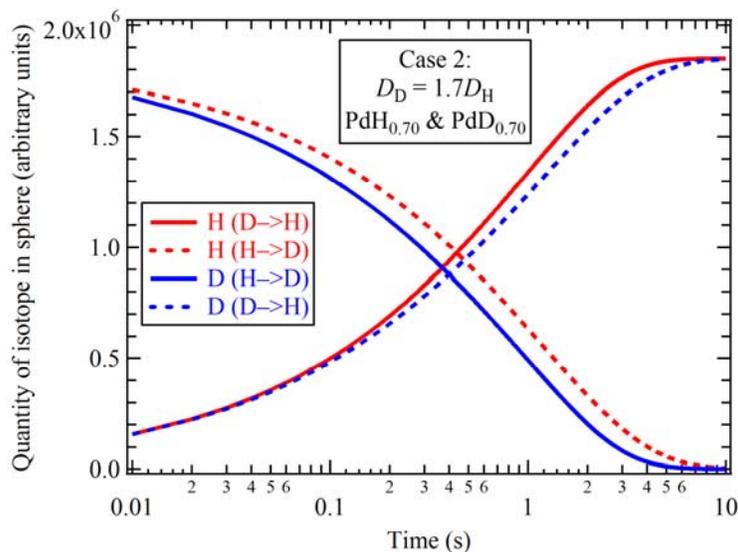
**Table 2: Test-run summary. For each case, both an H $\rightarrow$ D and a D $\rightarrow$ H exchange were simulated. The particle radius was 10  $\mu$ m, the temperature was 300 K and the simulation spanned ten seconds.**

	Stoichiometry PdH <sub>0.7</sub> and PdD <sub>0.7</sub>	Stoichiometry PdH <sub>0.7</sub> and PdD <sub>0.65</sub>
Diffusion rate: $D_D = D_H$	Case 1 Release of H = Release of D	Case 3 Release of H > Case 1
Diffusion rate: $D_D = 1.7D_H$	Case 2 Release of D > Release of H	Case 4 Release of H > Case 1



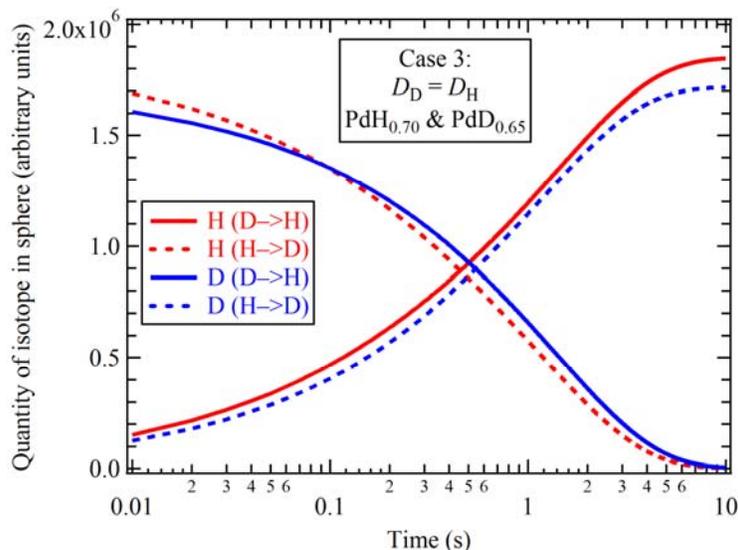
**Figure 4: Case 1. Because H and D are assigned identical diffusion rates and stoichiometries, there is no “isotope effect.”**

Case 2 involved changing the diffusion rate of deuterium to be 1.7 times the diffusion rate of hydrogen. Calculated are: the isotope release of H in an H→D simulation and the release of D in a D→H simulation. The results are shown in Figure 5. The biggest effect is that release of D in a D→H exchange becomes faster than the release of H in an H→D exchange. As demonstrated later, the faster release of deuterium due to the higher deuterium diffusion rate appears to be the biggest contributor to the “isotope effect.”



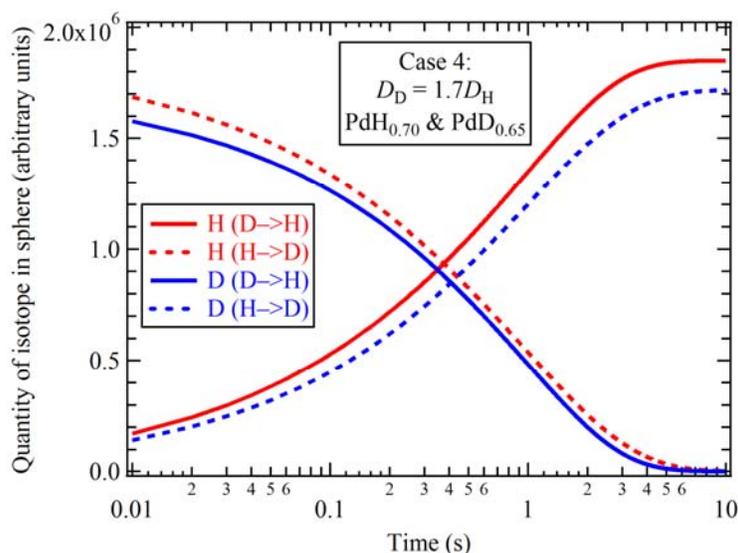
**Figure 5: Case 2. For this run the deuterium diffusion rate was increased to 1.7 times the hydrogen diffusion rate. Deuterium leaves the sphere in a D→H exchange faster (solid blue curve) than hydrogen leaves in a H→D exchange (dashed red curve).**

Case 3 examines effects of different stoichiometries. For this case, the diffusion rates were reset to those used in Case 1, but the stoichiometry was reduced from Pd D<sub>0.70</sub> to PdD<sub>0.65</sub>, which correspond to the stoichiometries at 299 K and 689,475 barye given by Wolfer et al. [14, Fig. 1]. The different stoichiometries for hydrogen and deuterium make it more difficult to compare the exchange rates because the quantity of one isotope released in an exchange is no longer equal to the amount of the other isotope consumed by the exchange. To facilitate comparison to the first two cases, the release of hydrogen in Cases 3 and 4 is highlighted. In other words, we compare the H→D reactions for Cases 3 and 4 to the reactions in Cases 1 and 2. Figure 6 shows the amounts of H and D in a β-Pd sphere for Case 3.



**Figure 6: Case 3.** For the D→H run, initially there is PdD<sub>0.65</sub> while for the H→D run, initially there is PdH<sub>0.70</sub> (hence the unequal end points in the upper right side of the figure). Note that the H release in the H→D reaction is faster than the D release in the D→H reaction.

Case 4 assigns different diffusion rates for H and for D along with different stoichiometries for PdH and PdD. Here we have two competing effects. The higher diffusion rate of D increases the rate at which D can leave the lattice in the D→H reaction: however, the lower stoichiometry of D in the pre-loaded PdD is decreased thereby reducing the quantity of D to be released.



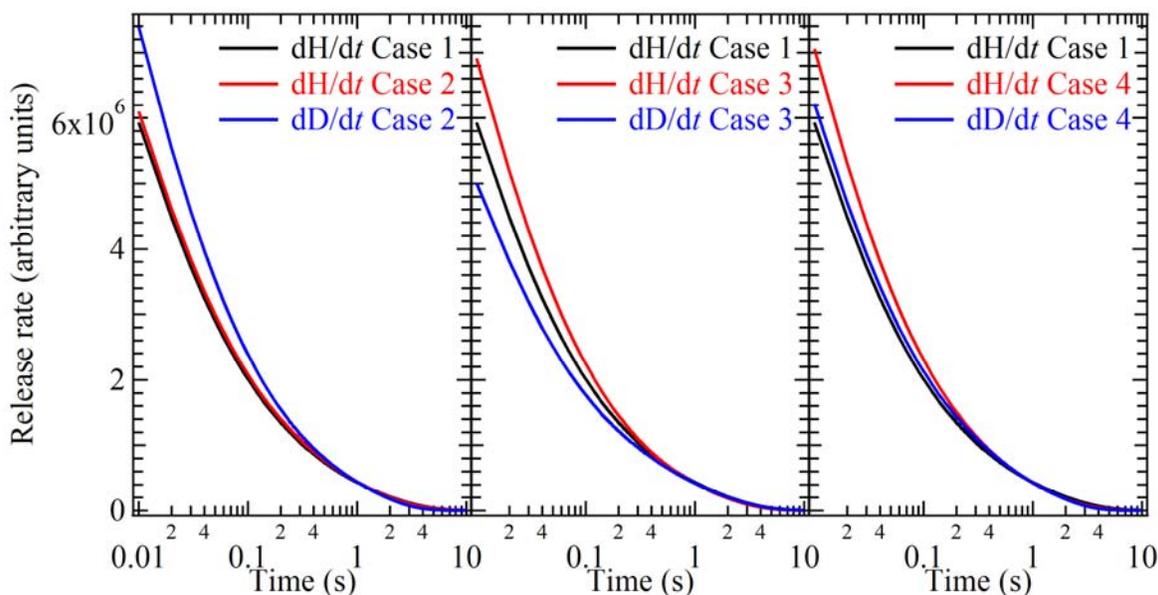
**Figure 7: Case 4.** Stoichiometry are PdD<sub>0.65</sub> and PdH<sub>0.70</sub> with diffusion rate for deuterium 1.7 times the diffusion rate for hydrogen (most applicable to a real exchange system). Due to the difference in starting stoichiometry for the red and blue curves it is difficult to define the relative rates.

To quantitatively compare the four cases, the rate of evolution of the initially loaded isotope is plotted in Figure 8. For the H→D reaction, the rate of H<sub>2</sub> evolution is plotted and for the D→H reaction, the rate of D<sub>2</sub> evolution is plotted. Case 1 is the black curve in all three plots to serve as reference.

Consider first the H→D reaction. For Case 2, increasing the deuterium diffusion rate ( $D_D = 1.7D_H$ ) notably increases the deuterium release rate, allowing faster H→D exchanges. For Case 3, decreasing the initial deuterium loading, PdD<sub>0.65</sub>, decreases the deuterium release rate. For Case 4, which is most representative of a real system, the two competing effects (higher diffusion rate increases release but reduced deuterium loading decreases release) largely cancel leaving the rate of deuterium evolution for Case 4 essentially equal to Case 1.

Now consider the D→H reaction. For Case 2, increasing the deuterium diffusion rate has only a slight effect on the hydrogen release rate. For Case 3, decreasing the final deuterium loading allows the uptake of deuterium to occur more rapidly thereby increasing the rate at which hydrogen is released. For Case 4, the evolution of hydrogen is essentially identical to Case 3.

Based on this analysis, it would appear that the reason why H→D exchange is faster than D→H exchange is due to the difference in stoichiometry of PdH and PdD under the same pressure and temperature.



**Figure 8: H or D isotope evolution from all cases compared. Case 1 is the black curve on all three plots to provide reference. Case 2 (increased deuterium diffusion rate) shows an increased deuterium evolution rate (blue curve). Case 3 (decreased deuterium loading) shows a decreased deuterium evolution rate, but increased hydrogen evolution rate (red curve). Case 4 shows the result of the two competing changes and H evolves faster than D.**

## Conclusion

A model for isotope exchange in palladium hydride spheres has been developed. It incorporates the most recent results for diffusion rates and for pressure-composition-temperature data available for H and D in Pd. An important part of this model is the interaction of the two isotopes on the interstitial sites of the Pd. This interaction is due both to the entropy of mixing and to elastic and electronic interactions between H and D. These effects are essential for any realistic model of isotope exchange in solid particles.

The model was applied to two example problems. The first investigated the time required for the solid exchange reaction as a function of time and temperature. These data can be used to determine if solid-state exchange might be a rate limiting factor at a given temperature and particle size. The second application was to investigate the role that solid exchange might play in the “isotope effect.” Differing stoichiometry of PdH and PdD in equilibrium with gas at a given temperature and pressure was the largest contributor to the isotope effect in solid particles.

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## Appendix A: SPEM Code

```
PROGRAM MAIN
! Predictor Corrector Method for Coupled Diffusion in Sphere
! Boundary conditions C(0)=C(1), C(N)=CHS or CDS
! IMPLICIT REAL*8 (A-H),REAL*8 (P-Z)
DIMENSION CH(0:200),CD(0:200),CHM(0:200),CDM(0:200)
DIMENSION AHH(0:200),AHD(0:200),ADH(0:200),ADD(0:200)
DIMENSION CTEMP(0:200)
OPEN(UNIT=3,FILE='TEST1.OUT',FORM='FORMATTED',STATUS='UNKNOWN')
WRITE(*,*)'Input sphere radius (micron)'
READ(*,*)RADIUS
WRITE(*,*)'Input temperature (K)'
READ(*,*)T
40 WRITE(*,*)'Input total exchange time(sec)'
READ(*,*)TIME
RADIUS=0.0001*RADIUS
N=199
NPO=N+1
DELR=RADIUS/(NPO)
DELT=.00001
DELTDT=DELT/2.
CHS=0.001
CDS=0.649
NTSTOP=TIME/DELT
DO 10 J=0,N
CH(J)=0.699
10 CD(J)=0.001
CH(N+1)=CHS
CD(N+1)=CDS
DO 12 NT=1,NTSTOP
! Perform Predictor Operation (half time step)
CALL DIFFXY(CH,CD,AHH,AHD,ADH,ADD,DELTDT,DELR,NPO,T)
CALL UPTWO(CH,CH,CHM,CD,AHH,AHD,N)
CALL UPTWO(CD,CD,CDM,CH,ADD,ADH,N)
! Perform Corrector Operation (full time step)
CALL DIFFXY(CHM,CDM,AHH,AHD,ADH,ADD,DELT,DELR,NPO,T)
CALL UPTWO(CH,CHM,CTEMP,CDM,AHH,AHD,N)
CALL UPTWO(CD,CDM,CDM,CHM,ADD,ADH,N)
DO 14 J=0,NPO,1
CHM(J)=CTEMP(J)
CHM(J)=(CHM(J)+CH(J))/2.
14 CDM(J)=(CDM(J)+CD(J))/2.
CALL DIFFXY(CHM,CDM,AHH,AHD,ADH,ADD,DELT,DELR,NPO,T)
CALL UPTWO(CH,CHM,CH,CDM,AHH,AHD,N)
CALL UPTWO(CD,CDM,CD,CHM,ADD,ADH,N)
12 CONTINUE
DO 13 J=0,NPO,1
```

```

POS=J*DELR*10000.
TEMP=CH(J)+CD(J)
13 WRITE(3,202) POS,' ',CH(J),' ',CD(J),' ',TEMP
202 FORMAT (1F7.2,A1,1F12.5,A1,1F12.5,A1,1F12.5)
STOP
END

```

```

SUBROUTINE DIFFXY(CH,CD,AHH,AHD,ADH,ADD,DELT,DELR,NPO,T)
DIMENSION CH(0:200),CD(0:200)
DIMENSION AHH(0:200),AHD(0:200),ADH(0:200),ADD(0:200)
! These are Einstein diffusion constants for H and D
DEINH=10**(-2.2620-3132.07/T)
DEIND=10**(-1.6772-3389.46/T)
DEINHW=DEINH/(8.314*T)
DEINDW=DEIND/(8.314*T)
! This is the derivative of excess chemical potential
! (Majorowski)
BETA=45050
DMUEE=BETA
DO 10 J=0,NPO
TCH=CH(J)
TCD=CD(J)
R=TCH+TCD
TCV=1.-R
DMUMIXHH=8.314*T*(1.-TCD)/(TCH*TCV)
DMUMIXDD=8.314*T*(1.-TCH)/(TCD*TCV)
DMUMIXDH=8.314*T/TCV
DHH=(DMUEE+DMUMIXHH)*TCH*TCV*DEINHW
DDD=(DMUEE+DMUMIXDD)*TCD*TCV*DEINDW
DHD=(DMUEE+DMUMIXDH)*TCH*TCV*DEINHW
DDH=(DMUEE+DMUMIXDH)*TCD*TCV*DEINDW
AHH(J)=DHH*DELT/(2.*DELR*DELR)
ADD(J)=DDD*DELT/(2.*DELR*DELR)
AHD(J)=DHD*DELT/(2.*DELR*DELR)
10 ADH(J)=DDH*DELT/(2.*DELR*DELR)
RETURN
END

```

```

SUBROUTINE UPTWO(CH,CHM,CHN,CDM,AHH,AHD,N)
! This is version for coupled diffusion spherical coordinates
! IMPLICIT REAL*8 (A-H),REAL*8 (P-Z)
DIMENSION CH(0:200),CHM(0:200),CHN(0:200),CDM(0:200)
DIMENSION AHH(0:200),AHD(0:200)

```

```

DIMENSION A(199),B(199),R(199),UDAG(199)
DO 10 J=1,N
A(J)=-AHH(J)
10 B(J)=1.+2.*AHH(J)
B(1)=1.+AHH(1)
! Calculate R array at beginning of time step
DO 11 J=1,N
R(J)=CH(J)+AHH(J)*(CH(J-1)-2.*CH(J)+CH(J+1))
& +2.*AHH(J)*(CHM(J+1)-CHM(J-1))/J
& +(AHH(J+1)-AHH(J-1))*(CHM(J+1)-CHM(J-1))/2.
& +2.*AHD(J)*(CDM(J-1)-2.*CDM(J)+CDM(J+1))
& +2.*AHD(J)*(CDM(J+1)-CDM(J-1))/J
& +(AHD(J+1)-AHD(J-1))*(CDM(J+1)-CDM(J-1))/2.
11 CONTINUE
R(N)=R(N)+AHH(N)*CH(N+1)
CALL TRIDAG (A,B,A,R,UDAG,N)
DO 12 J=1,N
12 CHN(J)=UDAG(J)
CHN(0)=CHN(1)
CHN(N+1)=CH(N+1)
RETURN
END

```

```

SUBROUTINE TRIDAG (A,B,C,R,U,N)
! This is from Numerical Recipes in Fortran
! IMPLICIT REAL*8 (A-H),REAL*8 (P-Z)
PARAMETER (NMAX=200)
DIMENSION GAM(NMAX),A(N),B(N),C(N),R(N),U(N)
! IF(B(1).EQ.0.)PAUSE
BET=B(1)
U(1)=R(1)/BET
DO 11 J=2,N
GAM(J)=C(J-1)/BET
BET=B(J)-A(J)*GAM(J)
! IF(BET.EQ.0.)PAUSE
U(J)=(R(J)-A(J)*U(J-1))/BET
11 CONTINUE
DO 12 J=N-1,1,-1
U(J)=U(J)-GAM(J+1)*U(J+1)
12 CONTINUE
RETURN
END

```