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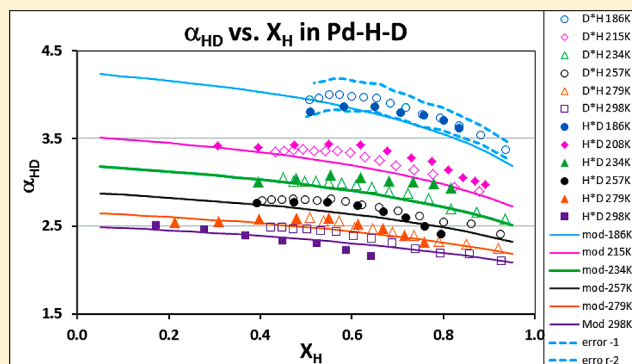# Separation Factors for Hydrogen Isotopes in Palladium Hydride

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ABSTRACT: This investigation examines how equilibrium pressures of single isotope metal–hydrogen systems can be used to determine the separation behavior of hydrogen isotopes in a mixed-isotope metal hydrogen system. The separation factor for a hydrogen–deuterium system, α_{HD}, describes the equilibrium hydrogen isotope partition between the solid and gaseous phases. Very few values of α_{HD} are reported for metals other than palladium, and the values for Pd are scattered with the origin of the scatter not fully understood. Wicke and Nernst and Trentin et al. have proposed models that relate α_{HD} to the ratio of single isotope equilibrium pressures and the isotopic composition of the solid. The approaches of these models and the resulting equations appear to differ; however, as will be shown here, they are identical. It also will be shown that Raoult's law, employed by both models, is not needed. This puts the model derivation on a firmer theoretical basis. New measurements of α_{HD} values are determined over a large temperature range and D/H ratio in β-phase Pd hydride, and they are compared with the model predictions, validating the model. Since experimental values for α_{HD} are often not available for other systems, while single isotope equilibrium pressures are available, the model provides a valuable tool for predicting separation factors. Moreover, the model can also be used to estimate separation factors involving the third hydrogen isotope, tritium.

1. INTRODUCTION

The isotope separation factor, α_{HD}, and equilibrium constant, K_{HD}, are two important parameters describing the equilibrium characteristics of mixed hydrogen isotope systems in metals. K_{HD} $(K_{HD} = P_{HD}^2/(P_{H2}P_{D2}))$ characterizes the isotopic partition of the three gaseous components, H_2, HD, and D_2, and is independent of the materials in contact with the gases. Urey and Rittenberg[1] calculated K_{HD} from statistical mechanics and found that it increases with temperature and approaches $K_{HD} = 4$ at high temperature. Their values for K_{HD} have been widely accepted for Pd–H–D systems and supported by experimentally measured K_{HD} values reported in the literature.[2–6]

The equilibrium separation factor is commonly written as $\alpha_{HD} = D_g H_s / D_s H_g$, where H_s $(=H/Pd)$ and D_s $(=D/Pd)$ are the atom ratios in the solid, while D_g $(=P_{D2} + 1/2P_{HD})$ and H_g $(=P_{H2} + 1/2P_{HD})$ are atom proportions of D or H in the gas, as given in terms of the partial pressures of the three molecular species. α_{HD} characterizes the hydrogen isotopic partition between the solid and gaseous phases, whereas K_{HD} describes the partition of H and D between the three gaseous components, H_2, D_2, and HD. It has been shown[7] that $\ln \alpha_{HD}$ varies linearly with reciprocal temperature $1/T$. However, reported values of α_{HD} for Pd–H–D are scattered even for a given phase,[5,8] e.g., the β-phase Pd hydride. The

origin of this scatter has been attributed to the dependence of α_{HD} on the total (H + D) concentration in the solid and the ratio of the isotopic fractions in the solid.[5,8]

There are very few values of α_{HD} reported for mixed isotope systems in metals other than in Pd, although the isotherms for many single isotope systems in metals are available. Theoretical expressions describing the thermodynamics of mixed isotope systems have been formulated, based on the thermodynamics of the respective single isotope systems. Formulations by Wicke and Nernst,[7] Brodowsky et al.,[8] and Trentin et al.[9] all show that the separation factor in a two-isotope system is a function of the ratio of the single isotope equilibrium pressures and the isotopic composition in the solid. They find that, at a given temperature, the larger the ratio of the equilibrium pressures in the single isotope systems and the larger the concentration of the isotope that has the greater chemical potential in its single isotope–metal system, the greater the separation factor. The approaches used in developing these models differ as well as the resulting expressions for α_{HD}, although it will be shown below that the equations given by Wicke and Nernst[7] and Trentin et al.[9] are identical.

It is intuitive that the partition of two H-isotopes in a metal results from the difference in their chemical potentials in the metal and equilibrium pressures of the single isotopes and their ratios, and this has been considered in the models mentioned above.[7−10] However, there is generally more than one M−H phase available in these systems, i.e., the dilute α-phase, the plateau region (α−β coexisting), and the high-concentration β-phase. In the plateau region, equilibrium pressures are nearly constant over a large range of H/Pd or D/Pd values, and as a result, more reliable values of α_{HD} can be obtained in this region. Pressures for the single-phase regions, α or β, are not only temperature dependent but also concentration dependent. Ambiguity in the selection of the appropriate pressure or concentration for use in a model causes the calculated α_{HD} values to differ widely.

Palladium absorbs a large amount of hydrogen and has a significant isotope effect, making it an attractive system for isotope storage/separation. Both the plateau region and the β-phase are attractive for their large capacities. Isotopic exchange behavior is slightly different in the plateau region than in the β-phase. For example, adding a dose of D_2 to β-phase Pd−H produces isotope exchange, without significantly changing the total concentration in the solid. However, adding a dose of D_2 to Pd−H in the plateau region causes the total content in the solid to increase as the system approaches equilibrium.[4] This study will focus on exchange in the β-phase Pd hydride where the total concentration remains relatively constant, and examine how α_{HD} depends on the ratio of the isotopes within the β-phase solid. Isotope exchange in the β-phase system is of technological value. For example, it provides a useful means for removing tritium from samples of aged Pd tritide without disturbing the He bubbles generated by tritium decay. Study of the bubbles is complicated by radiological concerns, and removal of the tritium without a change of phase may be important for retaining bubble characteristics.

Previously, a new Sieverts-type exchange method with a gas-sampling mass spectrometer was employed for varying and measuring the isotopic composition in mixed isotope Pd systems.[3,4,11] In the current investigation, isotope exchange experiments are carried out using the same approach but over a much larger extent of exchange; i.e., about 50% of the H or 85% of the D originally in the β-phase solid is exchanged using multiple doses of D_2 and H_2 addition. The experiments will examine exchange in both directions and then determine values of α_{HD} over a wide range of H/D compositions and temperatures in order to examine the dependence of α_{HD} on the isotopic ratio and to test the model predictions.

In the next part of this paper, we will discuss and compare the models proposed by Trentin et al.,[9] Brodowsky et al.,[8] and Wicke et al.[7] They all use the ratio of the equilibrium pressures of the two single isotopic−metal systems, i.e., the H−Pd and D−Pd systems. Although this study focuses on exchange behavior that takes place in the β-phase region, we will examine the difference in equilibrium pressure ratios in both the β-phase and the plateau regions and how they affect α_{HD} values obtained from the model. The calculated values of α_{HD} will then be compared with the new measurements.

2. THERMODYNAMICS OF HYDROGEN ISOTOPE EXCHANGE IN PD

The isotope separation factor is defined as

$$a_{HD} = \frac{\left(Y_{D2} + \frac{1}{2}Y_{HD}\right)X_H}{\left(Y_{H2} + \frac{1}{2}Y_{HD}\right)X_D} \tag{1}$$

Thus, the equilibrium α_{HD} is a function of five variables, Y_{D2}, Y_{H2}, Y_{HD}, X_H, and X_D, where the first three are the fractions of the three gaseous components (H_2, HD, and D_2) and the last two are the atom ratios in the solid. After adding a dose of H_2 to the D_2−Pd system in the plateau region, the total pressure, i.e., the sum of partial pressures of H_2, D_2, and HD, falls below the plateau pressure of the single isotope system of D_2−Pd but above that of H_2−Pd.[12] After adding a dose of H_2 to the system, the equilibrium partial pressures of the three gaseous components change and the total equilibrium pressure decreases as the fraction of H in solid, X_H, increases until the system reaches the β-phase. For the reverse case of adding a dose of D_2 to the H_2−Pd system, the total equilibrium pressure increases with X_D. In both cases, the total system pressure varies with the isotopic concentrations in the solid. The distribution of the two isotopes between the gas and solid phases is controlled by α_{HD}. In this paper, the dependence of α_{HD} on the isotopic composition in the β-phase region at different temperatures will be determined.

2.1. Models Relating α_{HD} and K_{HD} to Single Isotope Equilibrium Properties.
Trentin et al.[9] proposed a model that relates the separation factor to the ratio of equilibrium pressures in the single isotope−metal systems and to the isotopic contents in the solid. We will compare this with an earlier model of Wicke and Nernst.[7] For this purpose, it is convenient to repeat the major part of Trentin's derivation[9] and to clarify the role of the isotope activity in the solid solution. An explanation will be given on how the single isotopic pressure values are selected for use within the model, as well as on how the separation factor depends on the various parameters. A derivation of an expression for α_{HD} will be given in terms of pressures of the single isotope−metal systems and the isotopic content of the solid. This derivation gives the same final expression for α_{HD} as Trentin et al. or Wicke et al. but does not employ the approximation of Raoult's law. An explanation will be given on how the single isotopic pressure values are selected for comparison with the model, as well as on how the separation factor depends on the various parameters.

The following symbols will be used in description for hydrogen and similar symbols will be applied to deuterium.

μ^g_{H2}: H chemical potential in the gaseous phase in a mixed system

μ^s_H: H chemical potential in the solid phase in a mixed system

μ^o_{H2}: standard chemical potential of pure H_2 in the gaseous phase

μ^o_H: standard chemical potential of pure H in the solid phase

$Y_{H2} = P_{H2}/(P_{H2} + P_{HD} + P_{D2})$: molecular fraction of H_2 in the mixed gaseous phase

$Y_{D2} = P_{D2}/(P_{H2} + P_{HD} + P_{D2})$: molecular fraction of D_2 in the mixed gaseous phase

a_{H2} (a_{D2}): H_2 (D_2) activity in the mixed gaseous phase

a_H (a_D): H (D) activity in the solid phase

γ_H (γ_D): H (D) activity coefficient in the solid phase

Hs or H/Pd (Ds or D/Pd): molar ratio of dissolved H (D) to Pd in the solid phase

$X_H = Hs/(H_s + D_s)$: atomic fraction of isotopic H in the solid phase

$X_D = H_s/(H_s + D_s)$: atomic fraction of isotopic D in the solid phase

P_{H2}^{eq} (P_{D2}^{eq}): plateau pressure of a single isotope Pd–H$_2$ (Pd–D$_2$) system

P^{eq}: equilibrium pressure of a mixed H–D system

R_p: Ratio of the equilibrium pressures of P_{D2}^{eq}/P_{H2}^{eq} in single isotopic systems

H*D: for exchange direction starting from (H$_2$ + PdD)

D*H: for exchange direction starting from (D$_2$ + PdH)

From the thermodynamics describing single isotope–metal systems, such as H$_2$–PdH (or D$_2$–PdD), the following chemical potential equality holds at equilibrium

$$\mu_{H2}^g = 2\mu_H^s \qquad (2)$$

For a mixed isotopic system, the atomic fractions, X_H (X_D) and Y_{H2} (Y_{D2}), of the isotopes in the gas and solid phases are needed to describe the system. The H$_2$ (or D$_2$) activity in the gaseous phase is $a_{H2} = P^{eq}Y_{H2}$ (or $a_{D2} = P^{eq}Y_{D2}$) and in solid is $a_H = \gamma_H X_H$ (or $a_D = \gamma_D X_D$). Here γ_H and γ_D are the activity coefficients of H and D in solid. Thus, the chemical potentials in the gas and solid phases are

$$\mu_{H2}^g = \mu_{H2}^o + RT\ln(a_{H2}) = \mu_{H2}^o + RT\ln(P^{eq}Y_{H2}) \qquad (3)$$

$$\mu_H^s = \mu_H^o + RT\ln(a_H) \qquad (4)$$

At equilibrium, by inserting eqs 3 and 4 into eq 2, we have

$$\mu_{H2}^g - 2\mu_H^s = \left(2\mu_H^o - \mu_{H_2}^o\right) + RT\ln\left(\frac{a_H^2}{P^{eq}Y_{H2}}\right) \qquad (5)$$

Since

$$(2\mu_H^o - \mu_{H2}^o) = RT\ln(1/p_{H2}^{eq}) \qquad (6)$$

By inserting eq 6 into eq 5, we have

$$P^{eq}Y_{H2} = P_{H2}^{eq}a_H^2 \qquad (7)$$

Equation 7 indicates that the partial pressure of H$_2$ in the gaseous phase in a mixed isotope system is proportional to the activity of H in the solid multiplied by the factor of P_{H2}^{eq}, the equilibrium H$_2$ pressure in a single isotope system.

Similarly, $P^{eq}Y_{D2}$ and $P^{eq}Y_{HD}$ are the equilibrium partial pressures of D$_2$ and HD in the gas phase:

$$P^{eq}Y_{D2} = P_{D2}^{eq}a_D^2 \qquad (8)$$

The equilibrium constant K_{HD} is given as

$$K_{HD} = \frac{(P^{eq}Y_{HD})^2}{(P^{eq}Y_{H2}P^{eq}Y_{D2})} = \frac{(P^{eq}Y_{HD})^2}{(P_{H2}^{eq}P_{D2}^{eq}a_H^2a_D^2)} \qquad (9)$$

where $P^{eq}Y_{HD}$ is the equilibrium partial pressure of HD in the gas phase and the second equality is obtained by inserting eqs 7 and 8 into eq 9. The equilibrium partial pressure of HD is obtained from eq 9 as

$$P^{eq}Y_{HD} = \sqrt{K_{HD}(P_{H2}^{eq}P_{D2}^{eq})}\,a_Ha_D \qquad (10)$$

By inserting eqs 8–10 into eq 1, we obtain

$$\begin{aligned}
\alpha_{HD} &= \left(\frac{Y_{D2} + \frac{1}{2}Y_{HD}}{Y_{H2} + \frac{1}{2}Y_{HD}}\right)\left(\frac{a_H}{a_D}\right) \\[6pt]
&= \frac{P_{D2}^{eq}a_D + \frac{1}{2}\sqrt{K_{HD}(P_{H2}^{eq}P_{D2}^{eq})}\,a_H}{P_{H2}^{eq}a_H + \frac{1}{2}\sqrt{K_{HD}(P_{H2}^{eq}P_{D2}^{eq})}\,a_D} \\[6pt]
&= \left(\frac{P_{D2}^{eq}}{P_{H2}^{eq}}\right)\frac{2a_D + \sqrt{K_{HD}(P_{H2}^{eq}/P_{D2}^{eq})}\,a_H}{2a_H + \sqrt{K_{HD}(P_{D2}^{eq}/P_{D2}^{eq})}\,a_D} \\[6pt]
&= R_p\frac{2a_D + \sqrt{K_{HD}/R_p}\,a_H}{2a_H + \sqrt{K_{HD}R_p}\,a_D} \\[6pt]
&= R_p\frac{2(a_D/a_H) + \sqrt{K_{HD}/R_p}}{2 + \sqrt{K_{HD}R_p}\,(a_D/a_H)}
\end{aligned} \qquad (11)$$

Here $R_p = (P_{D2}^{eq}/P_{H2}^{eq})$.

Up to this point, the isotopic activities for H and D in solid in eqs 7–11 have not been defined. In the models of Trentin et al.,[9] Raoult's law was employed, and therefore, a_H and a_D were replaced by X_H, and X_D, respectively, without any discussion of the validity of the approximation. In the present derivation, the isotopic activity coefficients will be employed, i.e., γ_H and γ_D, respectively.

$$a_H = \gamma_H X_H \quad \text{and} \quad a_D = \gamma_D X_D$$

Although the isotopic activity coefficients, γ_H and γ_D, are not known, it is reasonable to assume $\gamma_H = \gamma_D$, since H and D occupy sites with similar surroundings within the Pd lattice. Therefore, we obtain

$$\frac{a_D}{a_H} = \frac{\gamma_D X_D}{\gamma_H X_H} = \frac{X_D}{X_H} \qquad (12)$$

Inserting eq 12 into eq 11, we obtain

$$\alpha_{HD} = R_p\frac{2(X_D/X_H) + \sqrt{K_{HD}/R_p}}{2 + \sqrt{K_{HD}R_p}\,(X_D/X_H)} \qquad (13)$$

Equation 13 has been derived from the model of Trentin[9] and Wicke et al.,[7] without using Raoult's law approximation. Although eq 13 is identical to Trentin's, it has not employed Raoult's law and is therefore on a firmer theoretical basis. This equation describes α_{HD} in terms of the ratio of the equilibrium pressures of the single isotope systems ($P_{D2}^{eq}/P_{H2}^{eq} = R_p$), the equilibrium constant (K_{HD}), and the isotopic fractions in the solid (X_H and X_D).

Wicke and Nernst[10] proposed the following expression for the dependence of α_{HD} on X_D:

$$\alpha_{HD} = \sqrt{R_p}\left(1 + \frac{X_D(\sqrt{R_p} + 1) - 1}{X_D\left(\frac{1}{2}\sqrt{K_{HD}R_p} - 1\right) + 1}\right)\left(1 - \frac{1}{2}\sqrt{K_{HD}}\right) \qquad (14)$$

Some symbols in eq 14 differ from those in the original publication,[10] but their definitions are consistent with those used by Trentin.[9] Equation 14 can be converted to eq 13 using $X_H + X_D = 1$:

$$
\begin{aligned}
\alpha_{HD} &= \sqrt{R_p}\left(1 + \frac{\left(X_D(\sqrt{R_p}+1)-1\right)\left(1-\frac{1}{2}\sqrt{K_{HD}}\right)}{X_D\left(\frac{1}{2}\sqrt{K_{HD}R_p}-1\right)+1}\right) \\
&= \sqrt{R_p} \\
&\quad \left(1 + \frac{X_D\sqrt{R_p}-\frac{X_D}{2}\sqrt{K_{HD}R_p}+X_D-\frac{X_D}{2}\sqrt{K_{HD}}-1+\frac{1}{2}\sqrt{K_{HD}}}{\frac{X_D}{2}\sqrt{K_{HD}R_p}-X_D+1}\right) \\
&= \sqrt{R_p}\,\frac{X_D\sqrt{R_p}+\frac{X_H}{2}\sqrt{K_{HD}}}{X_H+\frac{X_D}{2}\sqrt{K_{HD}R_p}} \\
&= R_p\,\frac{2X_D+\sqrt{K_{HD}/R_p}\,X_H}{2X_H+\sqrt{K_{HD}R_p}\,X_D}
\end{aligned}
$$

The last step shows that the equation of Wicke and Nernst[7] is identical with Trentin's, even though the latter[9] did not indicate that their model was identical with Wicke's.[7]

Brodowsky et al.[8] presented a model starting from the definition of α_{HD}:

$$
\alpha_{HD} = \frac{\left(P_{D2}+\frac{1}{2}P_{HD}\right)/\left(P_{H_2}+\frac{1}{2}P_{HD}\right)}{X_D/X_H} = \frac{\sqrt{P_{D2}}\,X_H}{\sqrt{P_{H2}}\,X_D}
$$

$$
\frac{\sqrt{P_{D2}}+\frac{1}{2}\sqrt{K_{HD}P_{H2}}}{\sqrt{P_{H2}}+\frac{1}{2}\sqrt{K_{HD}P_{D2}}} = \frac{k_D}{k_H}f
$$

$$
\left(\text{here: } f = \frac{\sqrt{P_{D2}}+\frac{1}{2}\sqrt{K_{HD}P_{H2}}}{\sqrt{P_{H2}}+\frac{1}{2}\sqrt{K_{HD}P_{D2}}}\right) \tag{15}
$$

Equation 15 is a general expression for α_{HD}, and K_D/K_H is the ratio of Sieverts' constants for the two isotopes D and H, which is constant for a given temperature. In this model, Brodowsky et al. used their experimental data to plot α_{HD} vs f which contains the pressures of H_2 and D_2. They reported a lower value of α_{HD} in the α-phase as compared with the plateau region. However, since α_{HD} depends on the isotope ratio and the total isotopic content in solid and since they did not include the parameters used in their calculations, it is not possible to verify or reproduce their results.

2.2. Model Application. *2.2.1. Determination of K_{HD}.* For the present application of eq 13, the K_{HD} values at given temperatures have been taken from Urey and Rittenberg.[13] A third-order polynomial fit to the four K_{HD} values of Urey[13] in the temperature range 100−400 K is given by

$$
\begin{aligned}
K_{HD} = &\; 2.545\times10^{-8}T^3 - 3.050\times10^{-5}T^2 + 0.01413T \\
&+ 1.094
\end{aligned} \tag{16}
$$

This expression is used to calculate K_{HD} for other temperatures examined in the model.

2.2.2. Dependence of α_{HD} on the Pressure Ratios. When using eq 13, both Trentin et al.[9] and Wicke et al.[7] chose equilibrium pressures in the solid phase coexistence region to calculate α_{HD}, although they did not justify their selection. Below we discuss the differences which result from choosing pressures in the $\alpha+\beta$ coexisting and in the β-phase regions.

2.2.2.1. Equilibrium Pressures in the $\alpha-\beta$ Coexisting Region. In the plateau region, where the two solid phases coexist, hysteresis (the pressure difference between absorption and desorption) introduces a difficulty in the selection of the appropriate pressures to employ. Four cases will be considered here: absorption for both H and D, desorption for both H and

D, H-absorption/D-desorption, and the reverse. For each case, the ratios of plateau pressures (P_{D2}^{eq}/P_{H2}^{eq}) were calculated using the enthalpies and entropies of absorption/desorption given by Wicke et al.[10] Figure 1 shows the dependence of α_{HD} on X_H at
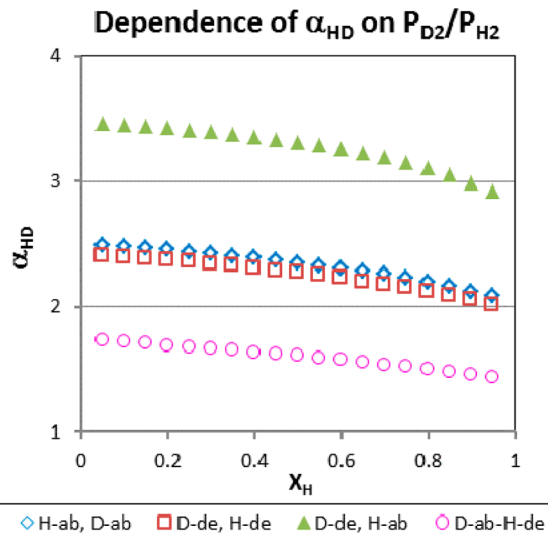

Figure 1. Dependence of calculated α_{HD} on X_H at 298 K for four different cases of H and D plateau pressures: both for absorption (open blue diamonds), both for desorption (open red squares), H-absorption/D-desorption (filled green triangles), and H-desorption/D-absorption (open purple circles).

298 K as determined by eq 13. It can be seen that the α_{HD} values are almost identical when both plateau pressures used are either both absorption or both desorption. By contrast, the α_{HD} values are significantly different if only one of the plateau pressures is for absorption and the other for desorption. It is also evident that α_{HD} decreases with X_H for all four cases. On the basis of these observations, we will use isotopic pressures for absorption in the remaining analysis. Table 1 lists the pressure ratio, P_{D2}^{eq}/P_{H2}^{eq} (ratio of absorption pressure),[10] and the values for K_{HD} at various temperatures;[13] these are used in the remainder of this paper.

Figure 2 shows the dependence of the calculated α_{HD} on X_H at various temperatures using the values of K_{HD} and P_{D2}^{eq}/P_{H2}^{eq} given in Table 1. Using these values, the dependences of α_{HD} on $1/T$ at fixed values of X_H, i.e., $X_H = 0.5$, 0.6, and 0.7, have been calculated and are shown in Figure 3. For each given X_H, a linear dependence of $\ln\alpha_{HD}$ on $1/T$ is apparent and described by the included fits. These values are in good agreement with those given by Wicke and Nernst[7] and Brodowsky and Repenning.[8]

2.2.2.2. Equilibrium Pressure Ratios in the β-Phase Region. In the β-phase of the Pd−H or Pd−D system, the equilibrium pressure increases markedly with the H or D concentration in the solid which complicates the selection of appropriate H_2 and D_2 pressures. Wicke and Nernst et al.[7] describe the linear dependence of $\ln P_{H2}$ on the H content in β-phase Pd−H by

$$
\ln P_{H2}\ (atm) = -A_H(T) + B_H(T)n \tag{17}
$$

where $A_H(T)$ and $B_H(T)$ are constants at a given temperature and n = H/Pd. A similar expression is given for the D−Pd system. Values of A and B are provided[10] for temperatures of 323, 298, 273, 243, and 195 K and are listed in Table 2 along with their uncertainties. Figure 4 shows the dependence of the

Table 1. P_{D2}^{eq}/P_{H2}^{eq} and from eq 13 and K_{HD} from the literature[7,14] Employed in the Present Research for the Calculations of Separation Factors α_{HD}, α_{HT}, and α_{DT}

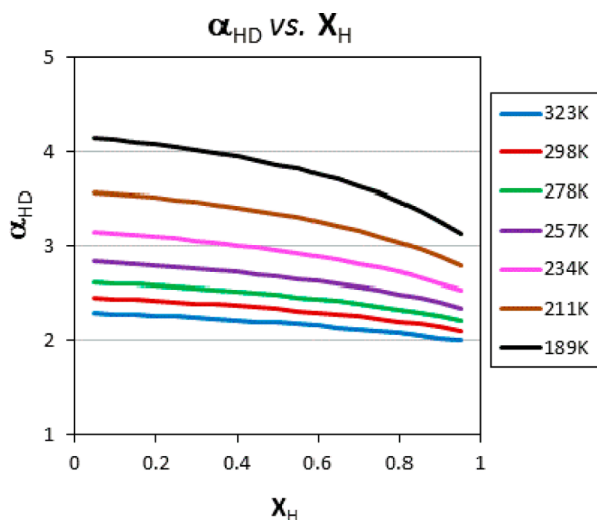| temperature (K)	189	211	234	257	278	298	323	50	100	200	300
P_{D2}^{eq}/P_{H2}^{eq}	12.36	9.61	7.76	6.52	5.70	5.10	4.53				
K_{HD} used here	2.84	2.98	3.11	3.21	3.29	3.35	3.41				
K_{HD}[14]								1.41	2.26	2.90	3.26
P_{T2}^{eq}/P_{H2}^{eq}	55.89	35.83	24.61	18.09	14.27	11.75	9.53				
K_{HT} used here	1.85	2.03	2.20	2.35	2.48	2.57	2.68				
K_{HT}[14]								0.33	0.95	1.94	2.58
P_{T2}^{eq}/P_{D2}^{eq}	5.07	4.06	3.47	3.01	2.70	2.47	2.24				
K_{DT} used here	3.60	3.66	3.72	3.77	3.82	3.86	3.90				
K_{DT}[14]								2.57	3.29	3.69	3.82

Figure 2. Dependence of calculated α_{HD} on X_H in a temperature range of 189−323 K.
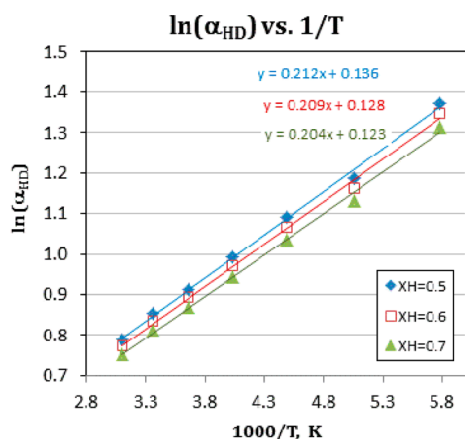

Figure 3. Calculated dependence of α_{HD} on temperature in the range 189−323 K for X_H = 0.5, 0.6, and 0.7.

coefficients A_H, B_H, A_D, and B_D on temperature as plotted using the data in Table 2, and the following equations describe the linear fits

$$A_H = 97.26 - 0.2144T, \quad B_H = 101.32 - 0.238T$$

$$A_D = 106.54 - 0.1983T, \quad B_D = 117.5 - 0.2418T$$

Values of A and B for H and D at the experimental temperatures used in the current work are obtained using these equations and are also listed in Table 2. The pressure

ratios, P_{D2}/P_{H2}, as calculated from A and B, are plotted in Figure 5. It can be seen that, at a given temperature, the P_{D2}/P_{H2} ratios vary with the isotope concentration in the solid. This could be a result of the uncertainty in A and B, since very small errors in A or B, as small as that indicated in Table 2, can lead to a significant error in the pressure ratio as calculated by eq 17. It can also be seen from Figure 5 that the average values of the pressure ratios P_{D2}/P_{H2} in this temperature range in the β-phase (averages of the solid lines) are very close to the pressure ratios in the plateau region (the dashed lines). In fact, the values from the plateau region best represent the difference in chemical potentials in the β-phase. Therefore, it is reasonable to use the ratio of P_{D2}/P_{H2} in this plateau region for all the model calculations and this approximation will be employed in the remainder of this article.

The dotted lines in Figure 5 show that the ratios of the two equilibrium pressures (P_{D2}/P_{H2}) decrease with increasing temperature. It can be seen from eq 13 that α_{HD} increases with this ratio of equilibrium pressures, R_p, which is why α_{HD} decreases with an increase in temperature.

2.2.3. Some Rules for the Dependence of α_{HD} on the Isotopic Content. From eq 13, the variation of α_{HD} with X_H, i.e., $(d\alpha_{HD}/dX_H)$, is given as

$$\frac{d\alpha_{HD}}{dX_H} = R_p \frac{(K_{HD} - 4) - 2\sqrt{K_{HD}R_p}X_H}{(2X_H + \sqrt{K_{HD}R_p} - \sqrt{K_{HD}R_p}X_H)^2} \quad (18)$$

Since $K_{HD} \leq 4$,[13] $(d\alpha_{HD}/dX_H)$ is always <0. That is, α_{HD} always decreases with X_H or increases with X_D. From eq 13, the following equations give the extreme cases as X_H or $X_D \to 0$

$$\lim_{X_D \to 0} \alpha_{HD} = \frac{1}{2}\sqrt{R_p K_{HD}} \quad (19)$$

$$\lim_{X_H \to 0} \alpha_{HD} = \frac{1}{2}\sqrt{R_p/K_{HD}} \quad (20)$$

For the case where K_{HD} = 4, eq 13 becomes

$$\alpha_{HD} = R_p \frac{2X_D + \sqrt{K_{HD}/R_p}X_H}{2X_H + \sqrt{K_{HD}R_p}X_D}$$

$$= \sqrt{R_p} \frac{2\sqrt{R_p}X_D + 2X_H}{2X_H + 2\sqrt{R_p}X_D}$$

$$= \sqrt{R_p} \quad (21)$$

It can be seen from eq 21 that the dependence of α_{HD} on X_H decreases when K_{HD} approaches 4. When K_{HD} = 4, α_{HD} is

Table 2. Equilibrium Pressure Coefficients for β-Phase Pd−H$_2$ and Pd−D$_2$ vs Temperature from Wicke et al.[7] and Those Calculated for the Current Experiments from Fits to Wicke's[7] Data for the Temperature Used in Current Experiments

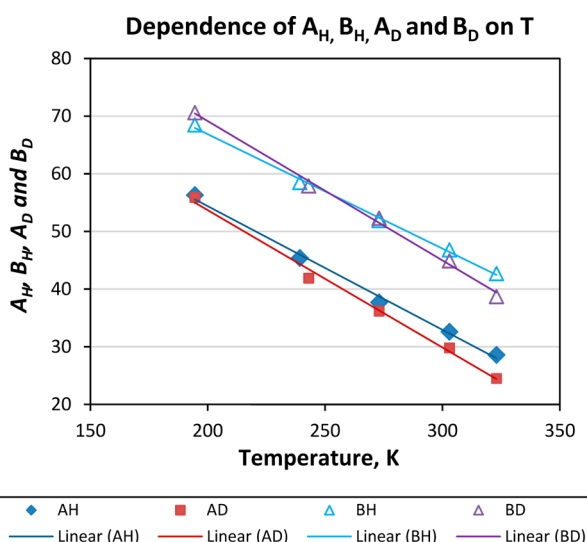|		H$_2$		D$_2$	
source	temp (K)	AH	BH	AH	BH
Wicke et al.[8]	323	29.1 ± 0.5	42.7 ± 0.6	24.5 ± 0.2	38.4 ± 0.3
	303	32.9	46.8	29.8 ± 0.3	44.7 ± 0.4
	273	38.2 ± 0.5	51.9 ± 0.4	36.2 ± 0.3	51.9 ± 0.4
	243			42.1 ± 0.2	57.8 ± 0.2
	239.2	45.5	58.5		
	194.5	56.6 ± 0.3	68.5 ± 0.3	55.9 ± 0.3	70.6 ± 0.2
current work	298	33.37	47.45	30.37	45.44
	278	37.66	51.41	35.13	50.28
	252	43.23	56.57	41.32	56.57
	234	47.09	60.14	45.60	60.92
	211	52.02	64.70	51.08	66.48
	189	56.74	69.06	56.32	71.80

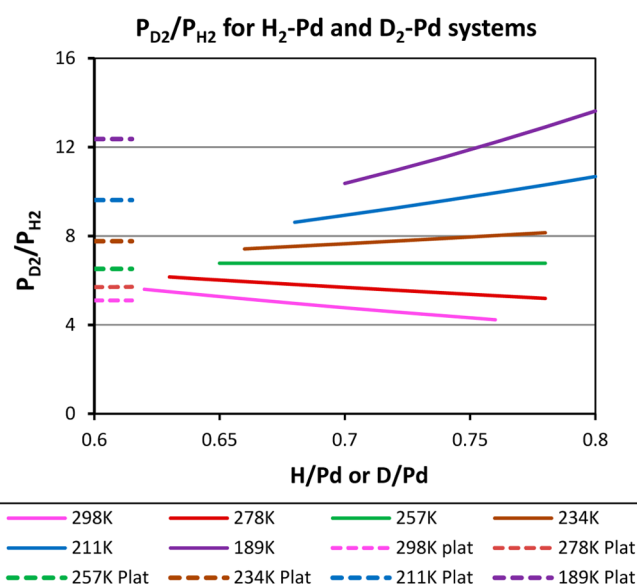**Figure 4.** Dependence of A_H, B_H, A_D, and B_D on temperature. Data from ref 7.

Figure 5. Dependence of pressure ratio, P_{D2}/P_{H2}, on the H or D contents in the β-phase. Solid lines are for P_{D2}/P_{H2} in the β-phase. The dotted lines are for P_{D2}/P_{H2} in the plateau region. Data in the plateau region are included for comparison.

independent of the solid composition. At most temperatures, however, $K_{HD} < 4$, as shown in Table 1, and we have

$$\lim_{X_D \to 0} \alpha_{HD} < \lim_{X_H \to 0} \alpha_{HD} \tag{22}$$

At a given temperature, K_{HD} is a constant. Since R_p is the ratio of the equilibrium pressures at that temperature, the only variable is X_H (since $X_D = 1 - X_H$). Thus, for a given temperature, the values of K_{HD} and P_{D2}^{eq}/P_{H2}^{eq} are fixed and the separation factor is a function of only the single variable X_H.

2.3. Model Application for H-T-Pd and D-T-Pd Systems. The separation factors α_{HT} and α_{DT} for H−T−Pd and D−T−Pd systems can be described by expressions similar to eq 13

$$\alpha_{HT} = R_p \frac{2X_T + \sqrt{K_{HT}/R_p}\,X_H}{2X_H + \sqrt{K_{HT}R_p}\,X_T} \tag{23}$$

$$\alpha_{DT} = R_p \frac{2X_T + \sqrt{K_{DT}/R_p}\,X_D}{2X_D + \sqrt{K_{DT}R_p}\,X_T} \tag{24}$$

where $R_p = P_{T2}^{eq}/P_{H2}^{eq}$ for eq 23 and $R_p = P_{T2}^{eq}/P_{D2}^{eq}$ for eq 24. Only four values of K_{HT} and three values of K_{DT} exist in the literature

in the temperature range 100−300 K. The available equilibrium pressures are for desorption, so we will use the pressure ratios for desorption.[14] Values of K_{HT} and K_{DT} at various temperatures are calculated from polynomial fits of the literature values[14] and are included in Table 1. Figure 6 shows the dependence of α_{HT} on X_H and α_{DT} on X_D as calculated from these values. It can be seen from Table 1 that, at a given temperature, $P_{T2}^{eq}/P_{D2}^{eq} > P_{D2}^{eq}/P_{H2}^{eq} > P_{T2}^{eq}/P_{D2}^{eq}$ and from Figures 2 and 6 that the magnitudes of the separation factors for the three systems, H−D, H−T, and D−T, are in the order of $\alpha_{HT} > \alpha_{HD} > \alpha_{DT}$.

3. EXPERIMENTAL DETERMINATION OF α_{HD} VALUES OVER EXTENDED COMPOSITION AND TEMPERATURE RANGES

A 2.5 g sample of Pd powder with a surface area of about 1 m^2/g, determined by the BET method, was used for the H−D exchange experiments. A sample with a large surface area was chosen for fast kinetics which leads to more reliable equilibrium values. Sets of H−D exchange experiments were carried out in
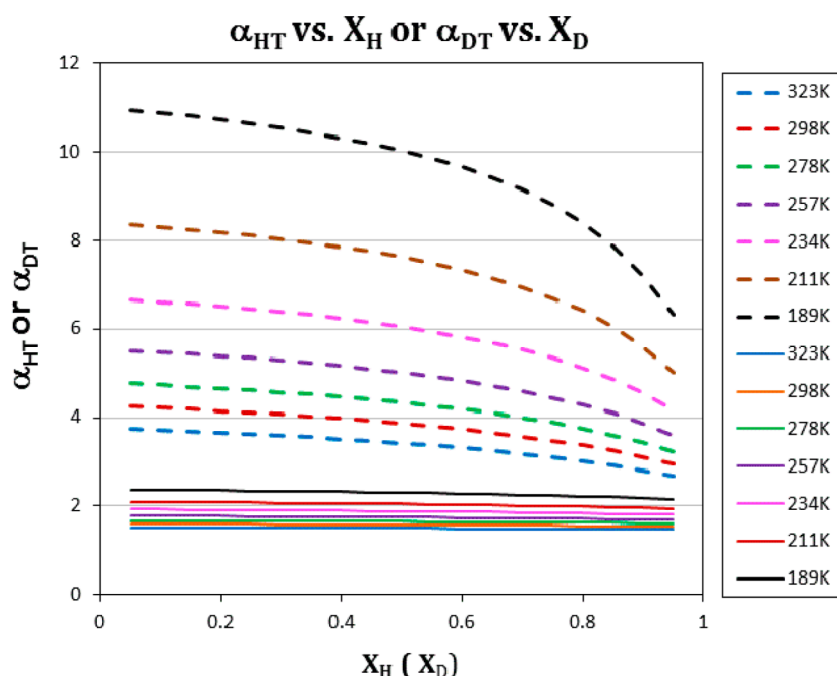
Figure 6. Dependences of α_{HT} vs X_H for the HT system (dashed lines) and α_{DT} vs X_D for the DT system (solid lines) in the temperature range 189–323 K.

both directions, H*D (H_2 + PdD) and D*H (D_2 + PdH), in the temperature range 189–298 K. A Sieverts apparatus was used to determine the amount of gas being absorbed/desorbed, as described previously.[3] Partial pressures of the three gaseous components, H_2, HD, and D_2, were measured using an SRS residual gas analyzer (RGA). A small amount of gas in the reaction chamber was allowed into the RGA through a custom-made crushed capillary gas flow restrictor. This arrangement ensured that a low pressure was maintained in the RGA ≤ 1.33 × 10^{-3} Pa (1 × 10^{-5} Torr), and the amount of gas removed from the reaction vessel was negligible.[4,3] Linear correlations between the RGA signal intensities and the partial pressures for H_2, HD, and D_2 were determined with different slopes for H_2 and D_2. Since pure HD is not commercially available, a specially designed experiment was carried out to determine the correlation between its ion current in the RGA and its partial pressure in the exchange chamber. In this experiment, fine Pt powder was employed to provide an active surface for the generation of equilibrium amounts of HD in situ from the isotope exchange at 298K by known amounts of H_2 and D_2. The expected equilibrium partial pressure of HD can be calculated from eq 25, given by Urey,[13] where the initial partial pressures of H_2 and D_2 are P_{H2}^i and P_{D2}^i, respectively, and the equilibrium partial pressure of HD is X

$$X^2/[(P_{H2}^i - X/2)(P_{D2}^i - X/2)] = 3.25 \qquad (25)$$

Twenty five gas mixtures were tested with known compositions of the isotopes of H_2 and D_2 with the total pressure in the range of 2 × 10^4 to 1 × 10^5 Pa, and the RGA responses to the gas samples were recorded. From the isotopic partial pressure (P^a) and RGA ion current (I^{ion}), their (P^a/I^{ion}) can be obtained. The (P^a/I^{ion}) relations have been previously used as the calibration in refs 3, 4, and 11. Bach et al.[15] reported a strong dependence of the isotopic ratio, P^a/I^{ion}, on the total pressure (P^{total}) in the gas chamber in the pressure range from 1 to 100 atm. In other words, the composition of the gas mixture in the exchange

chamber (the high-pressure chamber) may differ from that in the RGA (the low-pressure chamber) when the chambers are connected by a cramped-capillary. Bach et al.[15] concluded that this results from mass fractionation. In the current study, the measured isotopic values for P^a, I^{ion}, and P^{total} are used to determine if mass fractionation is a factor when P^{total} is between 0.2 and 1 atm. Figure 7 shows the dependence of the isotopic ratio of (P^a/I^{ion}) on the total pressures. Here the green line and symbols are for (P^a/I^{ion})$_{D2}$; the blue line and symbols are for (P^a/I^{ion})$_{H2}$; the red line and symbols are for (P^a/I^{ion})$_{HD}$; and the dashed blue line is for the average of the green and blue lines,
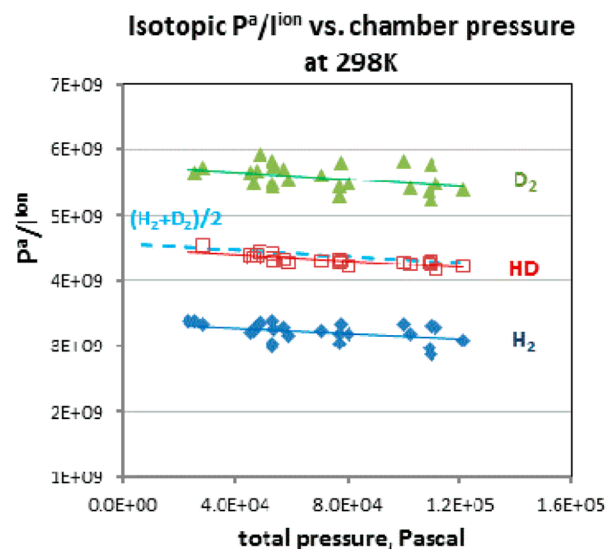

Figure 7. The dependence of the ratio of the partial pressure and ion current (P^a/I^{ion}) vs the total pressure in the exchange chamber. The blue symbols and line are for (P^a/I^{ion})$_{H2}$, the green symbols and line are for (P^a/I^{ion})$_{D2}$, the red symbols and line are for (P^a/I^{ion})$_{HD}$, and the dashed bright blue line is the average of the blue and green lines.

respectively. It can be seen that the (P^a/I^{ion}) ratios for H_2, D_2, and HD are essentially constant when the pressure is below 1×10^5 Pa, with a very small slope, i.e., (P^a/I^{ion}) decreases for H_2 ~1.2%. It also can be seen that the red symbols overlap with the dashed blue line in Figure 7, which validates the calibration for HD previously employed with the average of those of H_2 and D_2.[3,4]

Figure 8 shows the ratio of P^a/I^{ion} for H_2/D_2 (the red line) and H_2/HD (the blue line). The green line is based on data
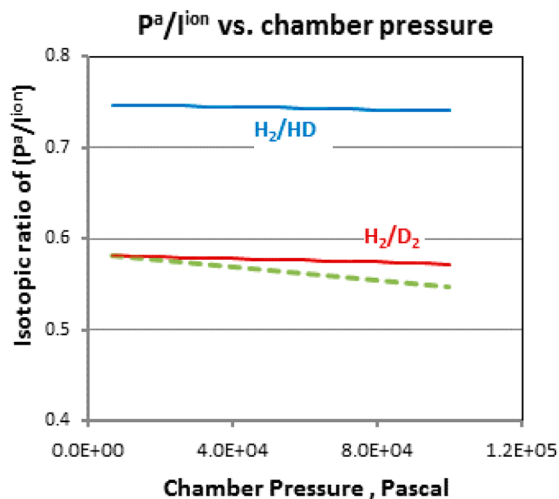
Figure 8. The dependence of the ratio of isotopic P^a/I^{ion} on the total pressure in the gas chamber at 298K. The blue line is the ratio of P^a/I^{ion} for H_2/HD, and the red line is for H_2/D_2. The dashed green line is for H_2/D_2, calculated using the literature data.[15]

from Bach et al.[15] for the (P^a/I^{ion}) ratio for H_2/D_2. A much stronger dependence of (P^a/I^{ion}) ratio for H_2/D_2 on P^{total} was observed in Bach's apparatus than in the current one. A possible reason for the different observations by Bach et al.[15] is in the difference in the cross-section areas of the crimped capillaries. In Bach's apparatus, the gas pressure in the exchange

chamber, i.e., the upstream of the crimped capillary, was ~1×10^7 Pa, whereas here it is 1×10^5 Pa, while the pressure in the downstream side of the capillary is similar for both, ~10^{-8} Pa. Thus, the cross-sectional area of the crimped capillary used in the current study is expected to be about 100 times larger than the one used by Back, which could result in significant differences in the gas flow pattern in the crimped capillaries.

It should be mentioned, based on the data in Figure 7, that, although mass fractionation is not observed in our pressure range, the P^a/I^{ion} values are scattered, which results in an uncertainty in the ratio of $(P^a/I^{ion})_{D2}/(P^a/I^{ion})_{H2}$ as large as 2.5%.

All isotopic exchange experiments were carried out at a constant temperature in the range 186−298 K for the H−D system. Experimental work was not conducted on tritium. During exchange experiments, the partial pressures of the three gaseous components were collected as a function of time and the isotopic contents in the solid were calculated by mass balance using ideal gas law. In the following figures, except in Figure 11, the isotopic concentrations in the solid, as well as the calculated α_{HD} and K_{HD}, are presented but not the concentrations in the gas phase.

4. RESULTS AND DISCUSSION

Time profiles for the solid composition variations for D*H exchange at 186 K, along with the derived K_{HD} and α_{HD} values, are shown in Figure 9. It can be seen that about half of the H_s was replaced by D_s after 14 exchange doses. The total isotope concentration in Pd, $(H_s + D_s)$, as shown by the brown line, remained nearly constant. Figure 10 shows the exchange results for the opposite exchange direction, H*D (189 K). Here the total isotope concentrations in the solid, $(H_s + D_s)$, increased slightly with X_H, as shown by the brown line in Figure 10. The larger maximum H-content for the plateau region in the single isotope H−Pd system as compared to the D-content in D−Pd is responsible for this increase. The K_{HD} value obtained from Figures 9 and 10 is about 2.6−2.9, which is close to the 2.75 calculated by Urey.[13]
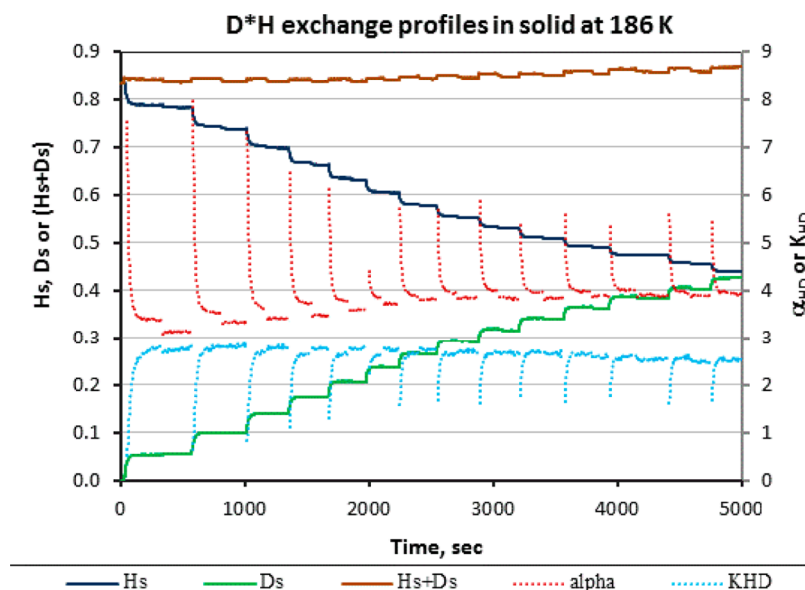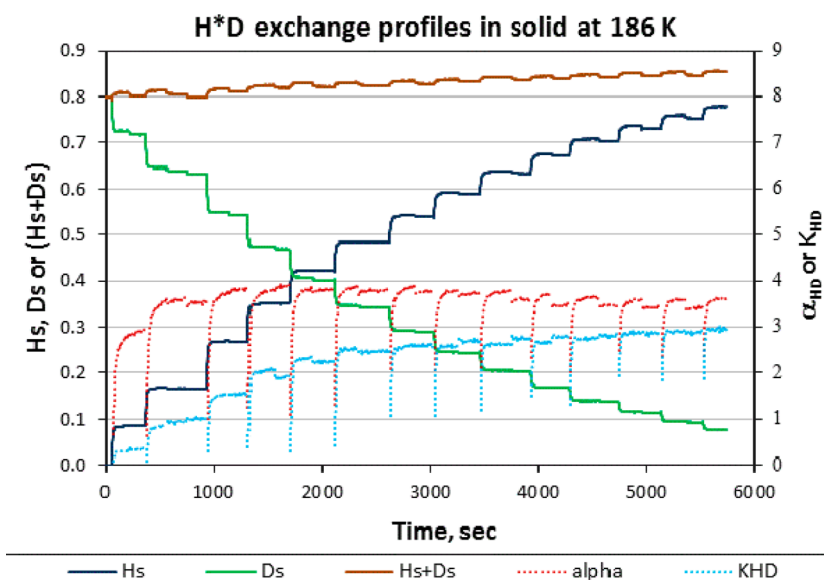
Figure 9. Exchange profiles showing solid compositions for D*H at 186 K for 14 doses of D_2. The blue and green lines are for H's and D's, respectively. The dotted lines are the values of K_{HD} (blue) and α_{HD} (red) during exchange.

Figure 10. Exchange profiles showing solid compositions for H*D at 186 K for 14 doses of H_2. The blue and green lines are for H's and D's, respectively, and the brown line is for (H's + D's). The dotted lines are the values of K_{HD} (blue) and α_{HD} (red) during exchange.

Figure 11 shows profiles for the gaseous composition variations occurring during the first dose for H*D at 186 K.

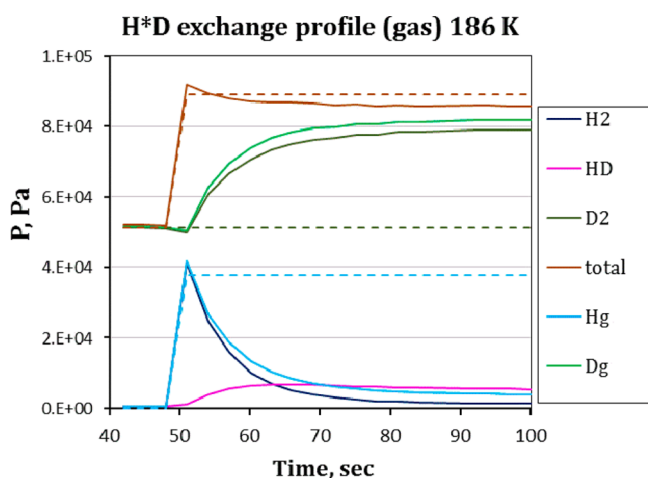**Figure 11.** Exchange profiles for gaseous species during the first dose of H*D. The solid lines are for H_2 (dark blue), D_2 (dark green), HD (purple), H_g (light blue), and D_g (light green). The dashed lines are for values of H_g, D_g, and their sum $(H_g + D_g)$ if no exchange occurred.

The solid lines are for the measured partial pressures for H_2 (dark blue), D_2 (dark green), and HD (purple) as well as the calculated Hg (bright blue) and Dg (bright green). At this temperature, $K_{HD} = 2.84$, as shown in Table 1. It can be seen from Figure 11 that, at equilibrium, the partial pressures of D_2 and HD are 7.98×10^4 and 4.48×10^3 Pa, respectively, while the pressure of H_2 is extremely small. Using the value of K_{HD} by Urey et al.[13] and the partial pressures for D_2 and HD from Figure 11, the P_{H2} should be 88 Pa (0.66 Torr). As reported earlier,[4] the error measured by the RGA could be as large as 700 Pa (5 Torr) or 2% of the readings, whichever is larger. Thus, the K_{HD} values calculated for the first five doses for H*D are smaller than their true values, due to the low accuracy of H_2 pressures in these doses. By contrast, this problem does not appear for the D*H direction, since the partial pressures of H_2
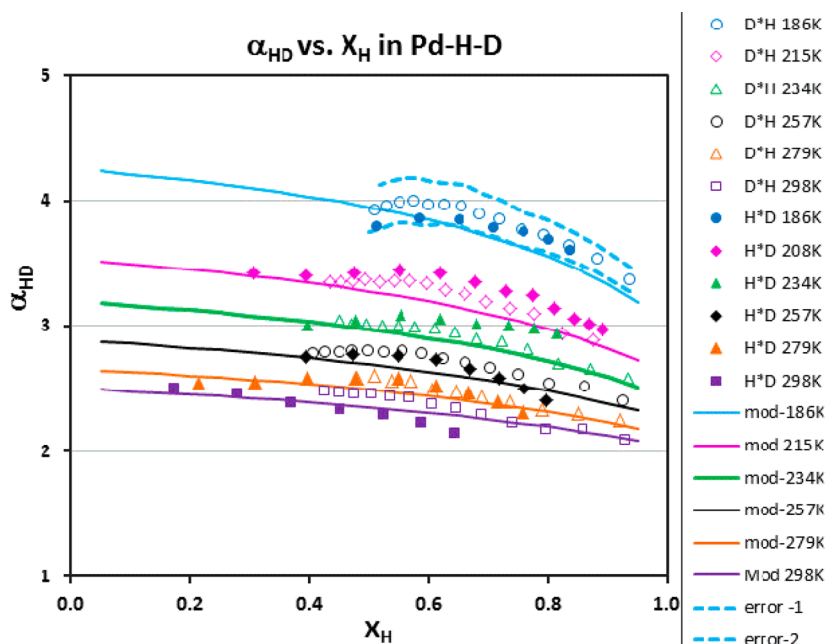
and D_2 are above this error range. Since $H_g = P_{H2} + 1/2P_{HD}$, rather than P_{H2}, is used for calculating α_{HD}, the errors in α_{HD} are relatively small in comparison with the errors in K_{HD}. This can be seen from Figures 9 and 10, where α_{HD} values are reasonably close for all doses in both exchange directions.

The dependence of α_{HD} on X_H at all temperatures for both exchange directions is shown in Figure 12. All solid lines in this figure are calculated using eq 13 and color coded by temperatures with the experimental data points, i.e., the blue for 186 K, the bright purple for 215 K, the green for 234 K, the black for 257 K, the orange for 279 K, and the dark purple for 298 K.

The error range for the exchange of D*H at 186 K is shown by two blue dashed lines, labeled as error-1 and error-2. The major source of error is considered to be the uncertainty of the ion currents from the RGA for H_2 and D_2, as shown by the relatively scattered data points in Figure 7. The average of ion-current ratio for I_{D2}/I_{H2} values in the temperature range 189–298 K was 1.53 ± 0.04. The error-1 and error-2 were calculated with ion currents of $I_{D2}/I_{H2} = (1.53 + 0.04)$ and $(1.53-0.04)$, respectively, about 2.5% uncertainty for I_{D2}/I_{H2}, for D*H at 189 K.

From Figure 12, the dependence of α_{HD} on the isotopic content in solid, X_H, is apparent, as predicted by the model. Even though there are some gaps between the calculated values and the experimental data points, the trend of decreasing α_{HD} with increasing X_H is clear. It should be noted that the determination of an experimental value for α_{HD} involves measurement of the partial pressures of all gaseous components and evaluation of the isotopic contents of solid components over 14 doses. Errors in each of these parameters and their accumulations over 14 doses as well as the uncertainty in calibration of the volume of the exchange chamber and thermal effect on the pressure readings will also contribute to the uncertainty of the measured α_{HD} values.

■ CONCLUSIONS

Thermodynamic information from the single isotopic systems, i.e., Pd–H_2 and Pd–D_2, can be used to determine isotopic distributions within the solid and the separation factors for

Figure 12. Dependence of α_{HD} on the fractional concentration of H in β-phase Pd—H—D: a comparison of experimental data points and model predicted values. Data points are color-coded by temperature: blue for 186 K, light purple for 215 K, green for 234 K, black for 257 K, orange for 279 K, and dark purple for 298 K. Open symbols for D*H and closed symbols for H*D. The dashed blue lines show the top and bottom of the primary uncertainty for D*H at 189 K; see text for details. The solid lines are for model calculated values.

mixed isotope systems. The equilibrium pressure for a single isotope reflects the strength of the interaction between the isotope and the host metal. The magnitude of the separation factor is a result of a difference in the interaction strengths between the host metal and the different isotopes. For H_2 and D_2 in the single-phase regions of the Pd system, i.e., the α or β phase, these equilibrium pressures vary significantly with the H or D concentration. Conversely, in the solid-phase coexistence region at a given temperature, each is essentially constant over a wide range of concentration. Thus, the pressure ratio, P_{D2}/P_{H2}, in this plateau region is nearly constant at a given temperature and can be used to determine the separation factor. Since the pressure ratio, P_{D2}/P_{H2}, decreases with increasing temperature, α_{HD} decreases with increasing temperature.

In this research, a model by Trentin et al., that uses thermodynamic concepts to estimate separation factors, has been examined. Another model developed by Wicke et al.[7] is shown here to be identical with that of Trentin et al.,[9] even though the two models' appearances and approaches are quite different. This is a result that the latter authors[9] did not mention. As the equation for α_{HD}, i.e., eq 13, was derived without the necessity of employing Raoult's law approximation, it places this equation for α_{HD} on a firmer theoretical basis. Values of α_{HD} are obtained from a series of isotope exchange experiments conducted in the β-phase Pd—H—D over the temperature range 186—298 K. These α_{HD} values are compared with those obtained from the model, and reasonable agreement is achieved.

From the model, it is clear that α_{HD} varies not only with temperature but also with the H/D ratio in the solid, a trend verified experimentally. This dependence explains why values of α_{HD} reported in the literature are scattered, as they are often reported without indicating the isotopic ratios in the solid. When $K_{HD} = 4$, i.e., at high temperature, α_{HD} is independent of the isotope ratio and equal to the square root of the equilibrium

pressure ratio of the single isotope systems P_{D2}/P_{H2}. The model shows that at a given temperature α_{HD} increases with the D concentration in the solid phase. It also provides a valuable tool for determining separation factors in mixed isotope systems using the more readily available plateau pressure data for the single isotopes.

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Notes
The authors declare no competing financial interest.

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