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Absorption isotherms for $H_2(D_2)$–$Pd_{0.8}Ag_{0.2}$ (198–323 K)

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ABSTRACT

Isotherms for H_2/D_2–$Pd_{0.8}Ag_{0.2}$ systems have been measured over a low temperature range, 198–323 K. Such low temperature data for this system have not been obtained previously. The absorption kinetics was found to be fast. The isotherms at low temperatures are compared with literature values at or above 313 K, as well as those for $H_2(D_2)$–Pd systems. The H/D isotope effect and the separation factors in the plateau range over $Pd_{0.8}Ag_{0.2}$ are calculated at various temperatures and discussed, based on the isotherms. Enthalpies are extracted from van't Hoff plots and compared with calorimetric values and the results from the literature for both absorption and desorption processes. A method is given for using isotherm information from single isotope systems to estimate the separation factor for the mixed isotope systems and this is a helpful tool.

The challenge of measuring absorption isotherms at low temperatures and low pressures is discussed. Sample pre-treatment, non-soluble impurity accumulation in an absorption process and thermal transpiration effects are examined.

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1. Introduction

Pd–Ag alloys are the most important Pd alloys with regard to H_2 solubility and diffusion because the $Pd_{0.77}Ag_{0.23}$ alloy is employed industrially as a H_2 purification membrane and as a hydrogen isotope separation alloy. Thermodynamic properties for the $H_2(D_2)$–$Pd_{0.8}Ag_{0.2}$ system have been reported in the literature only for the temperatures at 313 K or above [1–4]. Plateau pressures at temperatures below 313 K are under 1330 Pa, which is significantly lower than for Pd [3,5]. In this study the absorption pressure–composition isotherms (P–c–T) for $H_2(D_2)$–$Pd_{0.8}Ag_{0.2}$ in the temperature range of 198–323 K were measured using a Sieverts' type apparatus. Enthalpy values for these systems are calculated from van't Hoff plots and compared with those in the literature obtained using other methods.

One challenge for isotherm measurement in this temperature range is to obtain accurate pressure values. Correct pressure values depend on the sample pre-treatment before measurement and the effect of the accumulation of the non-soluble impurities in the source hydrogen, even for those of high-purity grade $H_2(D_2)$. Due to the large temperature differences between the sample chamber and the pressure gauges, thermal transpiration may also be a factor and must be considered.

2. Experimental

A two and one-half gram sample of $Pd_{0.8}Ag_{0.2}$ fine power (from Colonial Metals Inc., with surface area of 3.75 m^2/g) and high-purity H_2 and D_2 gases (both 99.9995% from Matheson) were used for the isotherm measurements. The sample vessel was carefully calibrated and purged with high-purity helium (99.999%) three times followed by three absorption–desorption-cycles before a P–c–T measurement. The sample was then evacuated by a Turbo pump at 443 K for at least 18 h before each isotherm measurement, which removes moisture and residual H_2 or D_2 and any other possible impurities accumulated from previous doses. After this evacuation, the residual gas pressure in the sample chamber was $<3 \times 10^{-7}$ Pa. No other pre-treatment was used on the sample.

The quantities of hydrogen absorbed in each dose were measured by the pressure changes in a carefully calibrated volume. Three MKS pressure gauges were used for pressure measurements: one 0–1000 Torr gauge to measure pressure in the dosing volume and two gauges, one of 0–1000 and one of 0–100 Torr, to measure the pressure in the sample vessel. The accuracy of all these gauges is 0.1% of full scale.

3. Results

The kinetics for H_2/D_2 absorption in $Pd_{0.8}Ag_{0.2}$ was fast, even at low temperatures. Fig. 1 shows an example of the absorption profile for a dose of D_2 absorption at 223 K, near the end of the plateau region. The absorption is completed in 20 min, similar to H(D)–Pd system.

Figs. 2 and 3 show the isotherms for H_2/D_2–$Pd_{0.8}Ag_{0.2}$ at various temperatures. It can be seen that the isotherms for both H_2–$Pd_{0.8}Ag_{0.2}$ (223–323 K) and D_2–$Pd_{0.8}Ag_{0.2}$ (198–323 K) have sloping plateaus which is common for alloys.

Fig. 4 shows the comparison of the isotherms at 323 K for H_2/D_2–$Pd_{0.8}Ag_{0.2}$ with those for H_2/D_2–Pd [6]. Those for

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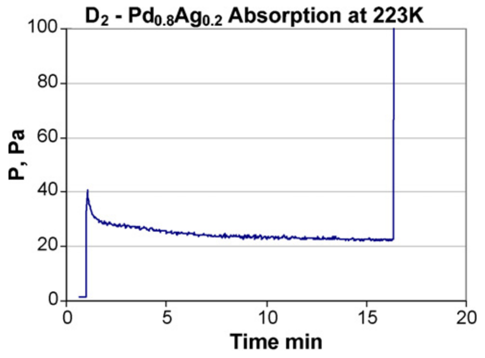

Fig. 1. An example of an absorption profile for a dose of D_2 in $Pd_{0.8}Ag_{0.2}$ at 223 K.

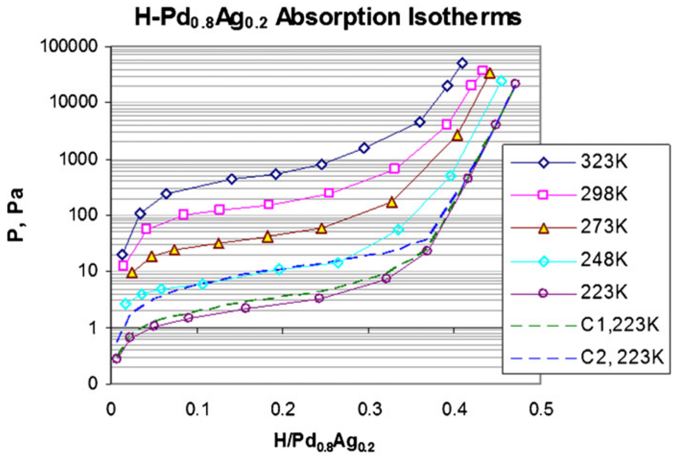

Fig. 2. H_2–$Pd_{0.8}Ag_{0.2}$ isotherms at 223–323 K.

H_2/D_2–Pd have flat plateaus with higher pressures and higher H(D)-capacities, which agrees with the literature [3].

In order to compare the isotherms measured in this work with those in the literature, desorption isotherms of Lasser et al. [2] for D_2–$Pd_{0.8}Ag_{0.2}$ are re-plotted in Fig. 5 from his data in the temperature range of 313–573 K. The absorption isotherm for D_2–$Pd_{0.8}Ag_{0.2}$ at 323 K from present work is included as the dashed green line, labeled as (323 Abs). The one from this work is very close to those of Lasser et al. [2] and hysteresis likely accounts for most of the difference. The desorption isotherms in Fig. 5 are less sloping than present one (323 Abs). The sample heat treatment before an absorption removes the dislocations in the lattice and this results in the equilibrium pressure increase and the plateau sloping in the absorption followed [7]. For present work the heat treatment before absorption (as described in Section 2) is believed to account for most of the extra sloping. For some systems the absorption isotherm shows more sloping than that for desorption, such as H–(Pd–Rh) and H–V systems [8,9]. It is not clear if this accounts for the extra sloping for the absorption isotherm for H(D)–$Pd_{0.8}Ag_{0.2}$ system.

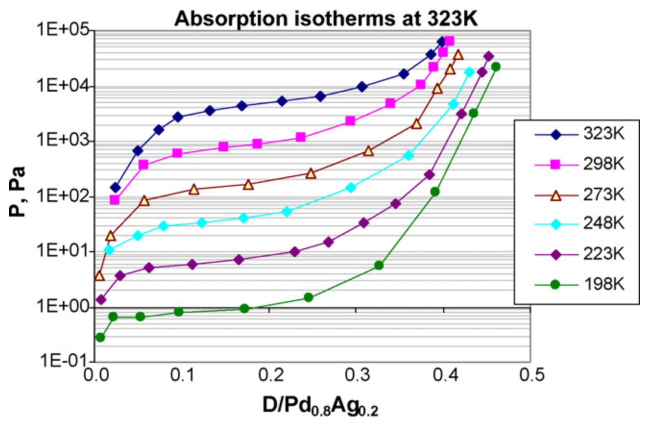

Fig. 3. D_2–$Pd_{0.8}Ag_{0.2}$ isotherms at 198–323 K.

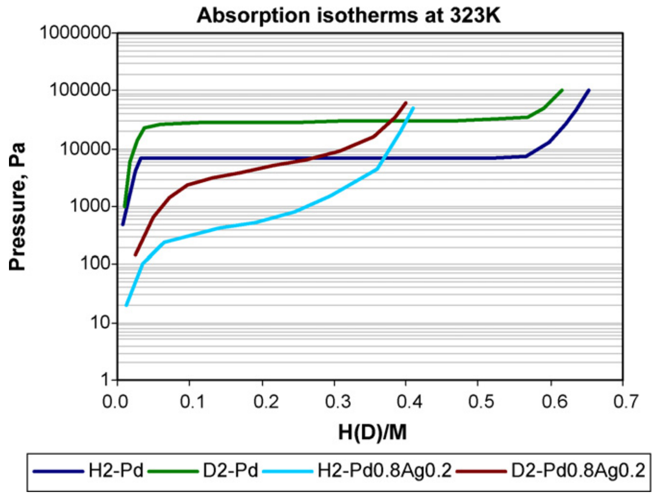

Fig. 4. The comparison of the absorption isotherms at 323 K for H_2/D_2–$Pd_{0.8}Ag_{0.2}$ with those for H_2/D_2–Pd.

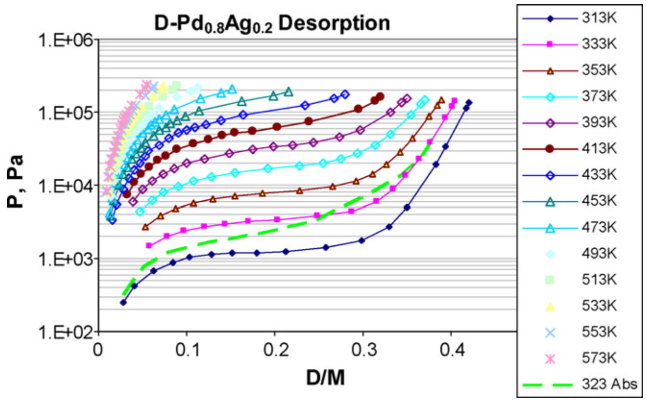

Fig. 5. Desorption isotherms for D_2–$Pd_{0.8}Ag_{0.2}$ re-plotted from data measured by Lasser et al. [2].

The mid-point plateau pressures for H_2/D_2–$Pd_{0.8}Ag_{0.2}$ systems at different temperatures are listed in Table 1. In the plateau region the H–D separation factors for a mixed isotope system can be determined from the plateau pressures of the single isotope systems by the following equation [10]:

$$\alpha = \left(\frac{P^{\circ}_{D_2}}{P^{\circ}_{H_2}}\right)^{0.5} \tag{1}$$

Here $P^{\circ}_{H_2}$ and $P^{\circ}_{D_2}$ are the plateau pressures of single isotope systems of H_2–$Pd_{0.8}Ag_{0.2}$ and D_2–$Pd_{0.8}Ag_{0.2}$, respectively. The calculated α

Table 1
H_2–D_2 isotope effects on $Pd_{0.8}Ag_{0.2}$ in a temperature range of 223–323 K.

Temperature (K)	P_{H_2} (Pa)	P_{D_2} (Pa)	$(P_{D_2}/P_{H_2})^{0.5}$	$\log((P_{D_2}/P_{H_2})^{0.5})$
323	732	3857	2.30	0.361
298	200	1091	2.34	0.369
273	39	266	2.60	0.416
248	10	79	2.80	0.448
223	1	10	2.89	0.460

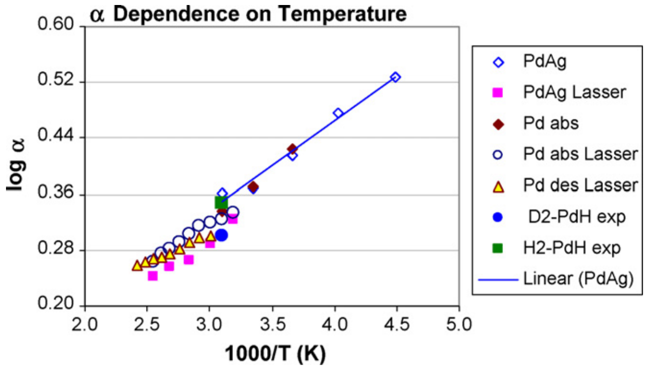

Fig. 6. The dependence of separation factor ln(α) on the temperature for $H_2/D_2–Pd_{0.8}Ag_{0.2}$ (blue diamonds are from this work, pink squares are from Lasser et al. data [2]), H_2/D_2–Pd absorption (brown diamonds are from this work and [12], blue circles are from Lasser and Klatt [13]), and H_2/D_2–Pd desorption (yellow triangles from Lasser and Klatt [13]). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

values at different temperatures are listed in Table 1 and plotted in Fig. 6. A linear correlation can be seen in this figure between log(α) and $1/T$. The separation factor α has larger values at lower temperatures, which agrees with those for other metal systems reported in the literature [11]. Some α values calculated from the literature isotherms for $H_2/D_2–Pd_{0.8}Ag_{0.2}$ desorption [2] and H_2/D_2–Pd absorption and desorption [6,12,13] are included in this figure for comparison. Experimental α data calculated from the definition $\alpha = (D_g/D_s)/(H_g/H_s)$ for the H–D–Pd system in plateau region at 323 K [14] are included in Fig. 6 with the legend of "H_2–PdD exp" to denote the case where H_2 is added to a system containing D and the legend of "D_2–PdH exp" to denote the reverse case. Here the subscripts "g" and "s" denote quantities in the gas and solid-Pd phases, respectively, and $D_g = P_{D_2} + 1/2P_{HD}$ and $H_g = P_{H_2} + 1/2P_{HD}$. It can be seen that values of α for the $H_2/D_2–Pd_{0.8}Ag_{0.2}$ and H_2/D_2–Pd systems and that those calculated from Eq. (1) and the experimental data are very similar. The enthalpy for H–D separation calculated from the linear fit to the absorption data in Fig. 6 is 2.5 kJ/mol-H(D). There appears to be no difference between values for absorption and desorption and there is no mention of any difference in the literature. The small difference shown in this figure could result from experimental error.

The thermodynamic meaning of α is of interest, e.g., the correlation of α with the chemical potentials of H_2 and D_2 in a given metal system. For the present case of $H_2–D_2$ in $Pd_{0.8}Ag_{0.2}$ in the plateau region the value of α relates to the difference of chemical potentials for the single isotope systems. According to following thermodynamic relations [15] for a plateau region of a metal–hydrogen system:

$$\begin{aligned} 1/2 ln\, P_{D_2} &= \frac{1/2\Delta\mu_{D_2}}{RT} = \frac{\Delta H_D}{RT} - \frac{\Delta S_D}{R} \\ 1/2\ln P_{H_2} &= \frac{1/2\Delta\mu_{D_2}}{RT} = \frac{\Delta H_H}{RT} - \frac{\Delta S_H}{R} \end{aligned} \qquad (2)$$

Together with Eq. (1) we have:

$$\ln\alpha = \frac{1}{2}(\ln P_{D_2} - \ln P_{H_2}) = \frac{\Delta H_D - \Delta H_H}{RT} - \frac{\Delta S_D - \Delta S_H}{R} \qquad (3)$$

It can be seen from Eq. (3) that $(\Delta H_D - \Delta H_H)$ and $(\Delta S_D - \Delta S_H)$ are the enthalpy and entropy for the H–D separation in a plateau region, respectively. Equation (3) should apply to other H–metal systems as well. It is a useful tool for estimating α, since the literature contains a significant amount of data on isotherms of H(D) in metal systems, but very few experimentally determined values of α.

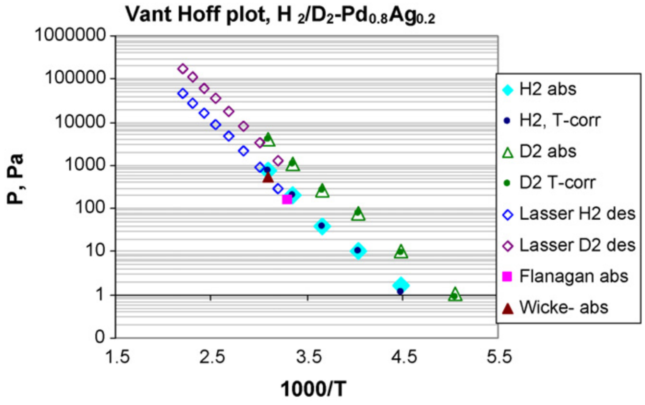

Fig. 7. The van't Hoff plot for $H_2/D_2–Pd_{0.8}Ag_{0.2}$.

Fig. 7 shows van't Hoff plots for both $H_2–Pd_{0.8}Ag_{0.2}$ and $D_2–Pd_{0.8}Ag_{0.2}$ using the plateau pressure values listed in Table 1. Literature values [1–4] are included for comparison, where the "Lasser H_2 des" and "Lasser D_2 des" [1,2] are for desorption of $H_2–Pd_{0.8}Ag_{0.2}$ and $D_2–Pd_{0.8}Ag_{0.2}$, respectively; "Flanagan H_2 abs" [3] and "Wicke H_2 abs" [4] are for absorption of $H_2–Pd_{0.8}Ag_{0.2}$, respectively. The van't Hoff plots from the data in this study are linear over the measured temperature range and fit in with those reported in the literature very well.

Enthalpy values calculated from the van't Hoff plots for the present H_2 and D_2 absorption results are listed in Table 2, along with those from Lasser's [1,2] isotherm data. It can be seen that the enthalpy values from Lasser's data are higher than those from this work, which is reasonable since Lasser's values are for desorption. Calorimetric enthalpy values from plateau regions are believed to represent the true equilibrium values without hysteresis. The average enthalpies calculated from the absorption and desorption data using P–c–T method [1,2,13] are close to these calorimetric values. Calorimetric enthalpies for the H_2/D_2–Pd systems are included in Table 2 for comparison [6].

Considering the correlation between plateau pressure variations and the difference between reaction enthalpies for H_2–Pd and $H_2–Pd_{0.8}Ag_{0.2}$ systems, we can use the following equation [15]:

$$\Delta H_2 - \Delta H_1 = \frac{1}{2}RT\ln\frac{P_1}{P_2}$$

Here the subscripts "1" and "2" stand for the quantity for the H_2–Pd and $H_2–Pd_{0.8}Ag_{0.2}$ systems, respectively. Using the P_1 and P_2 in Fig. 4 gives a $(\Delta H_2 - \Delta H_1)$ of 3 kJ/mol-H. If the H_2–Pd calorimetric values are used as a reference, the enthalpy for $H_2–Pd_{0.8}Ag_{0.2}$ should be about 22 kJ/mol-H, a value between those obtained using the P–c–T method, included in present work, Lasser's work [1,2], and the calorimetric value from the literature [3].

It should be pointed out that the effect of non-soluble impurities in the source gas, even with high-purity, on the measured pressure can be significant at low temperatures. At the end of an absorption cycle the impurity concentration in the sample vessel is much higher than that in the source gas since the impurity accumulates in the gas phase with each dose. At low temperature the sum of

Table 2
Enthalpy values (kJ/mol-H(D)) for $H_2/D_2–Pd_{0.8}Ag_{0.2}$ calculated from van't Hoff plots. Enthalpy values for H_2/D_2–Pd are included for comparison.

	Methods	H_2	D_2
$H_2/D_2–Pd_{0.8}Ag_{0.2}$ absorption	P–c–T	19.9	17.6
$H_2/D_2–Pd_{0.8}Ag_{0.2}$ desorption [1–2]	P–c–T	21.1	21.1
$H_2–Pd_{0.81}Ag_{0.19}$ [3]	Calorimetry	23.4	–
H_2/D_2–Pd [6]	Calorimetry	19.1	17.3

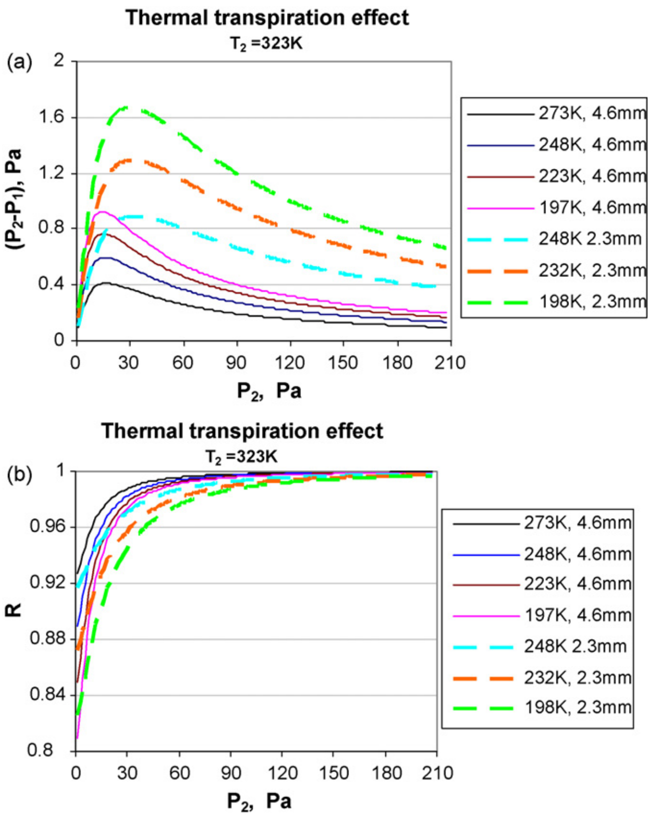

Fig. 8. Thermal transpiration correction for $T_2 = 323$ K and $d = 4.6$ mm, 2.3 mm. (a) $(P_2 - P_1)$ vs. P_2. (b) R vs. P_2.

partial pressures of the impurities can be comparable to the partial pressure of H_2. An example of the impurity effect on the isotherm at 223 K is calculated and presented in Fig. 2. The dark purple line is the measured isotherm with H_2 purity of 99.9995%, the green dashed lines (C1, 223 K) and the blue dotted line (C2, 223 K) are calculated for the cases for the purities of 99.999% and 99.99%, respectively. This impurity effect is apparent for the case in Fig. 2; however, it is much less significant when the equilibrium hydrogen pressures are higher.

Since the isotherms considered here are at lower temperatures, i.e. the sample was in a low temperature chamber while the pressure readings were taken from the gauges at 323 K, corrections for thermal transpiration should be considered. The following equation [16] was used to calculate the corrections:

$$R = \frac{P_1}{P_2} = \frac{\alpha_{\mathrm{He}}(\phi_g X)^2 + \beta_{\mathrm{He}}(\phi_g X) + R_m}{\alpha_{\mathrm{He}}(\phi_g X)^2 + \beta_{\mathrm{He}}(\phi_g X) + 1} \qquad (4)$$

All symbols/variables in the equation defined as follows [16]: P_1, equilibrium pressure (Torr) at low temperature T_1 (K); P_2, equilibrium pressure (Torr) at high temperature T_2 (K); $R_m = (T_1/T_2)^{0.5}$; d, internal diameter (in mm) of tubing which connects T_1 and T_2; $X = P_2 d$; $\alpha_{\mathrm{He}} = 3.70(1.70 - 0.0026(T_2 - T_1))^{-2}$; $\beta_{\mathrm{He}} = 7.88(1 - R_m)$; $\phi_g = 1.44$ (for H_2 and D_2).

The thermal transpiration corrections calculated from Eq. (4), with $T_2 = 323$ K and $d = 4.6$ mm as in this experiment, are plotted in Fig. 8a as ΔP $(=P_2 - P_1)$ vs. P_2 in Fig. 8b as R $(=P_1/P_2)$ vs. P_2. Data for $d = 2.3$ mm (thick dashed lines) are included for comparison with those for $d = 4.6$ mm (thin lines). It can be seen from these figures that:

- The corrections are more significant for smaller size tubing which connects the sample chamber at low temperature and the gauge at higher temperature.
- The corrections (R) are more significant at lower P_2.
- There is a maximum value of ΔP which agrees with the literature [16].

The plateau pressure values with the thermal transpiration corrections are shown in Fig. 4 for both H_2 and D_2 systems, labeled as "H_2 T-corr" and "D_2 T-corr", by using the correction factors calculated from Eq. (1). It can be seen that the corrections for the conditions in this experiment, i.e. the connecting tubing size (4.6 mm) and current ΔT (125 K) range, are insignificant.

4. Conclusions

Absorption isotherms for the H_2/D_2–$Pd_{0.8}Ag_{0.2}$ systems over a low temperature range, 198–323 K, have been measured. These data have not been previously reported in the literature. The absorption kinetics was found to be very fast, similar to H(D)–Pd system. The isotherms and isotope separation factors at low temperatures are compared with those at or above 313 K from the literature, as well as those for $H_2(D_2)$–Pd systems. An expression is given for the separation factor for a mixed isotope system in terms of the equilibrium plateau pressures for the single isotopes. Procedure for scaling the H–D isotope effect from Pd to $Pd_{0.8}Ag_{0.2}$ is also discussed. Absorption enthalpies are calculated from van't Hoff plots, giving values which agree reasonably well with those in the literature. They are also very close to those for H–D–Pd systems.

It is a challenge to measure low pressure isotherms, e.g., as low as 0.3 Pa. The sample pre-treatments, non-soluble impurity accumulations in an absorption process and thermal transpiration corrections are considered and discussed. These factors can influence the accuracy of absorption isotherms measured at low temperature.

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