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## Calorimetric enthalpies for palladium–hydrogen (deuterium) systems at H(D) contents up to about $[H]([D])/[Pd] = 0.86$

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**Abstract.** The enthalpies for the reaction of gaseous hydrogen and deuterium with palladium have been measured as a function of  $[H]/[Pd]$  and  $[D]/[Pd]$  atomic ratios up to 0.865 and 0.85, respectively, in the temperature range 298–194.5 K using a differential-heat-flow low-temperature calorimeter; pressure–concentration isotherms have been measured simultaneously. The calorimetric ( $\alpha + \beta$ ) two-phase enthalpies for the Pd–H and Pd–D systems at 298 K are  $\Delta H_H = -18.6 \pm 0.3 \text{ kJ (mol H)}^{-1}$  and  $\Delta H_D = -17.1 \pm 0.3 \text{ kJ (mol D)}^{-1}$ , and the corresponding entropies determined from the calorimetric enthalpies and the absorption plateau pressures are  $\Delta S_H = -46.2 \pm 0.5 \text{ J (mol H)}^{-1} \text{ K}^{-1}$  and  $\Delta S_D = -47.5 \pm 0.5 \text{ J (mol D)}^{-1} \text{ K}^{-1}$ . These  $\Delta H_{H(D)}$ - and  $\Delta S_{H(D)}$ -values are in agreement with the previously reported values and also with values determined in the literature from van't Hoff plots of the plateau pressures.

The calorimetrically determined enthalpies  $\Delta H_{H(D)}$  for solution in the  $\beta$ -phase regions of both systems become less exothermic in an almost linear fashion with increasing H(D) content, independently of temperature. At the same H(D) content, the  $\Delta H_H$ -values for the Pd–H system are slightly more exothermic than the  $\Delta H_D$ -values for the Pd–D system. Enthalpies of almost the same magnitude are obtained from the desorption data. The corresponding entropies,  $\Delta S_{H(D)}$  for solution in the  $\beta$ -phase region of both systems have a tendency to decrease gradually with increase in H(D) content independently of temperature; however, there is no marked difference between the magnitudes of the  $\Delta S_{H(D)}$ -values of the two systems. The dependences of the calorimetric enthalpies for hydrogen (deuterium) solution on H and D contents in the ranges  $0.70 < [H]/[Pd] < 0.86$  and  $0.70 < [D]/[Pd] < 0.85$  can be expressed by the temperature-independent relations  $\Delta H_H \text{ (kJ (mol H)}^{-1}) = 46.71[H]/[Pd] - 50.38$ , and  $\Delta H_D \text{ (kJ (mol D)}^{-1}) = 49.69[D]/[Pd] - 50.75$ . The variations in  $\Delta H_{H(D)}$ -values with H(D) content are in agreement with that calculated from van't Hoff plots of the previously reported relative chemical potentials of hydrogen and deuterium at low temperatures. The present calorimetric data determined by gas-phase measurements do not offer support for the generation of any 'excess heat' up to  $[D]/[Pd] = 0.85$ , beyond that which is expected from the chemical reaction because the values determined calorimetrically are almost the same as those derived from van't Hoff plots.

### 1. Introduction

The anomalous phenomenon of 'excess heat' generation in 'cold-fusion' reactions observed during electrolysis in a  $D_2O$ –LiOD solution containing a palladium cathode [1, 2] has been questioned. Many experimentally unknown factors exist, e.g. the electrical quantities introduced into the electrolysis up to the onset of heat generation, the action of the Li ions contained in the electrolyte on the electrode surface, and the variations in electrolysis current density and electrode overpotential, during electrolysis. The occurrences of excess

heat generation, although observed with poor reproducibility, seem to be closely related to highly deuterated Pd,  $[D]/[Pd] > 0.83$  [3–7], where the electrical resistance of the deuterated Pd electrodes should still be high, even though the resistance passes through the maximum near  $[D]/[Pd] = 0.75$  [8, 9].

In order to determine whether the excess heat results from some ‘unknown new phenomena’, i.e. ‘cold nuclear fusion’, or from ‘known chemical and physical effects’, it is important to obtain calorimetrically determined enthalpies of reaction of deuterium with Pd in high-concentration regions for comparison with the Pd–H system. There are, however, few thermodynamic and calorimetric data available in high-concentration regions for either system [10–13].

In addition to the observations of the excess heat generation during electrolysis, i.e. during dynamic conditions, calorimetric enthalpies obtained using a gas-phase method, together with pressure  $p$ –concentration  $c$  isotherm measurements, should also reflect the dynamic conditions which occur during the hydriding or dehydriding processes. In particular, if the key factor for the excess heat generation is a ‘high deuterium content’ in palladium, the gas-phase method is rather free from the unnecessary complications mentioned above for observing any heat generation compared with the electrochemical methods.

Wicke and Nernst [10] have determined data on hydrogen and deuterium absorption and desorption by Pd using  $p$ – $c$  isotherm measurements at pressures up to about 0.1 MPa and at temperatures down to 194.5 K, where the  $[H]([D])/[Pd]$  ratios which are obtained by extrapolating from the low-pressure measurements to higher pressures give a value of about 0.85. The relative partial molar enthalpies  $|\Delta H_{H(D)}|$  in the  $\beta$ -phase region calculated from van’t Hoff plots decrease almost linearly with increasing  $[H]([D])/[Pd]$ .

Tkacz and Baranowski [11] determined the absorption of hydrogen by Pd within the gaseous hydrogen pressure range 1–12 kbar at temperatures between 298 and 338 K using a piston–cylinder-type of high-pressure generation device. In contrast with the results of Wicke and Nernst [10], the enthalpies for solution of hydrogen from  $[H]/[Pd] = 0.87$  to  $[H]/[Pd] = 0.995$  show an anomalously large exothermicity with increase in hydrogen content, although the relative chemical potential  $\Delta\mu_H$  increases markedly with increasing hydrogen content. From these data the estimated amount of heat is about  $0.6 \text{ kJ (cm}^3 \text{ Pd)}^{-1}$ . This heat is much smaller than that of about  $173 \text{ kJ (cm}^3 \text{ Pd)}^{-1}$  which has been observed as the ‘excess heat’ calculated by assuming that the excess heat output of  $2 \text{ W (cm}^3 \text{ Pd)}^{-1}$  is continued for 24 h during the electrolysis [4, 6].

Recently, Flanagan *et al* [12] have measured enthalpies for the reaction of gaseous hydrogen and deuterium with Pd over a  $[H]([D])/[Pd]$  range up to about 0.77 at 298 K using a twin-cell, differential-heat-flow calorimeter combined with a Sieverts  $p$ – $c$  isotherm measurement. The results for  $\beta$ -hydride formation enthalpies are  $-19.1 \text{ kJ (mol H)}^{-1}$  and  $-17.3 \text{ kJ (mol D)}^{-1}$ , and these calorimetric enthalpies are in good agreement with values determined from van’t Hoff plots of the plateau pressures [14]. The calorimetric enthalpies  $|\Delta H_{H(D)}|$  in the  $\beta$ -phase region of Pd–H and Pd–D systems decrease more steeply with increasing H(D) content than do the results of Wicke and Nernst [10] which were determined from van’t Hoff plots.

In order to understand the true nature of the previously observed ‘excess heat’, the aim of the present study was to obtain calorimetric information about the enthalpies of reaction of gaseous hydrogen and deuterium with palladium at high H(D) contents at temperatures down to 194.5 K by a combination of twin-cell differential-heat-flow calorimetry and  $p$ – $c$  isotherm measurements.

## 2. Experimental details

The twin-cell differential-heat-flow calorimeter [12, 15–17] used in this study is the Setaram low-temperature calorimeter (model BT2.15 II) operable in the temperature range from 77 to 473 K and with a sensitivity of about 20  $\mu\text{W}$ . The system for temperature control and data acquisition and analysis is based on a IBM PS/V 2410 desktop computer. The two identical hydriding cells, i.e. the reaction (sample) vessel (of volume  $V_s$ ) and reference vessel (of volume  $V_R$ ) of the calorimeter are connected to a Sieverts  $p$ – $c$  isotherm measurement apparatus constructed of all stainless steel tubes and vessels of SUS 316. Pressures were measured by two pressure gauges: one is an MKS 0–10 000 Torr pressure transducer for relatively low-pressure measurements, and the other is a strain-gauge type of transducer capable of measuring pressures up to about 7.5 MPa. The system is also capable of being evacuated to about  $4 \times 10^{-7}$  Pa.

The heats of reaction can be calculated from

$$\Delta H_{H(D)} = \Delta h_{H(D)}(V, T) / \Delta n_{H(D)} \quad (1)$$

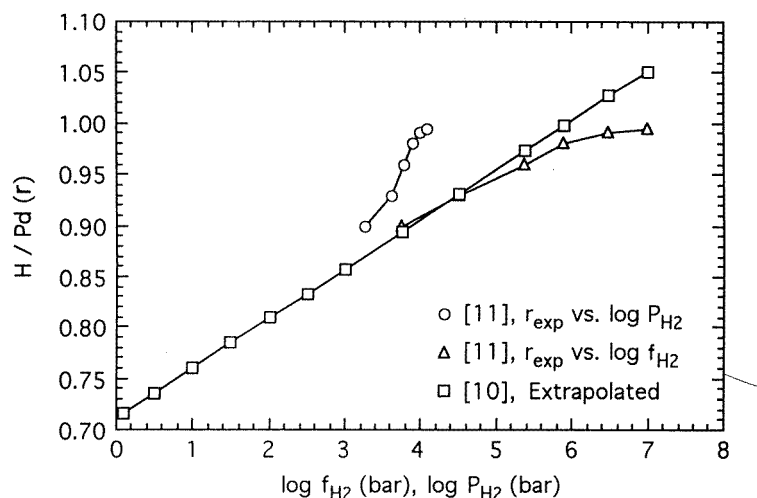
where  $\Delta h_{H(D)}$  is the heat due to absorption or desorption of H(D) by the solid; the twin-cell differential calorimeter measurement cancels out on general principles two heat effects, because  $V_s = V_R$ : one is a ‘ $Vdp$ ’ effect which is significant in the higher-pressure region, and the other is a heat transfer effect from the gas reservoir which is not at the calorimeter temperature.  $\Delta n_{H(D)}$  is the number of moles of H(D) absorbed or desorbed by the solid in the  $p$ – $c$  isotherm measurements, and for each dose is given as  $\Delta n_{H(D)} = 2\{V_d \Delta p_d - [V_c + (V_s + V_R)T_R/T_e]\Delta p_s\} / RT_R$ , where  $V_d$  is the volume of the dosing tube,  $\Delta p_d$  is the pressure difference within the dosing volume before and after a given dose and  $\Delta p_s$  is the pressure difference within the reaction and reference vessels, i.e. in the volume  $V_s + V_R$ ,  $V_c$  is the volume of the connection tube and  $T_e$  is the measuring temperature. In general, in  $\alpha + \beta$  plateau regions,  $\Delta p_s$  is small, and precise values of  $\Delta n_{H(D)}$  can be obtained. However, in the high-pressure  $\beta$ -single-phase region the pressures are large and, consequently, the values of  $\Delta p_s$  are large, leading to errors in  $\Delta n_{H(D)}$ ; so it is important that the value of  $V_s + V_R$  is as small as possible. The volume of the dosing tube in this study was  $V_d = 157.74 \text{ cm}^3$ ; the sample and reference vessels (inner diameter, 12.0 mm) had the volumes  $V_s = 9.07 \text{ cm}^3$  and  $V_R = 9.06 \text{ cm}^3$ , respectively; the volume of the connection tube was  $V_c = 11.16 \text{ cm}^3$ . The temperature  $T_R$  of the dosing tube was 305 K.

Prior to the experiments, the calorimeter was checked with a standard electrical calibration heater. It was confirmed that the calorimeter can detect almost entirely the heat supplied by the calibration heater, and there was good linearity between the supplied heat and detected heat. In the experiments on the Pd–D system, about 1.5 kg of granular  $\text{Fe}_{0.94}\text{Ti}_{0.96}\text{Zr}_{0.04}\text{Nb}_{0.04}$  alloy was used as a  $\text{D}_2$ -storage system in a 1000 ml type 316 stainless steel cylinder vessel. The purity of the  $\text{D}_2$  was 99.5%. After the alloy material had absorbed  $\text{D}_2$  gas at 273 K and up to about 1.5 MPa, the  $\text{D}_2$  pressures required up to about 7.5 MPa could be adjusted in the apparatus by electrically heating the vessel to about 493 K.

8.0002 g of fully annealed Pd foil (99.99% wt%; a bench mark specimen supplied by Tanaka Kikinzoku Kogyo KK for the research projects of NHE) which had been cut to a thickness of 50–60  $\mu\text{m}$  and an area of about 2 mm $\times$ 2 mm was used as a sample in the reaction vessel by mixing with Cu foil (5.0001 g) of almost the same dimensions. An amount of Cu, whose volume was the same as that of the Pd+Cu in the reaction vessel, was placed in the reference vessel in order to improve the heat conduction. Before putting the Pd and Cu specimens into the vessels, the former was chemically etched with a solution

of 2:2:1  $\text{H}_2\text{SO}_4 : \text{HNO}_3 : \text{H}_2\text{O}$  and the latter was also etched with a dilute  $\text{HNO}_3$  solution in order to remove any oxides from the surfaces. In order to obtain an highly active state for the  $p$ - $c$  isotherm measurements and calorimetry, the vessels were completely outgassed at about  $4 \times 10^{-6}$  Pa and at 573 K, and then the samples were exposed to hydrogen gas at about  $p_{\text{H}_2} = 0.1$ –3 MPa for 10 min. Subsequently, the vessels were slowly cooled in ice-water, and dehydriding was then accomplished by reheating at the same temperature. This hydriding–dehydriding treatment was repeated more than ten times.

In addition to the calorimetry at 298 K, low-temperature calorimetry below 273 K was carried out by controlling temperatures with a Setaram CS-32 controller under cooling with a liquid-nitrogen flow. To protect the calorimeter tubes against any risk of moisture condensation, the tubes were exposed to a nitrogen atmosphere at about 200 mbar. The variation in the temperature before the calorimetry was  $\pm 0.01$  K to  $\pm 0.02$  K at all the measurement temperatures.



**Figure 1.** Comparison of experimental high-pressure solubility [11] and extrapolated solubility from low-pressure measurements [10] in palladium at 298 K: ○, experimental solubility against hydrogen pressure of  $\log p_{\text{H}_2}$  [11]; △, experimental solubility against hydrogen fugacity of  $\log f_{\text{H}_2}$  [11]; □, extrapolated solubility from low-pressure measurements against hydrogen pressure of  $\log p_{\text{H}_2}$  [10].

For the high-pressure experiments, as described above, it is generally difficult to obtain precise  $p$ - $c$  isotherm data even for Pd–H(D) systems, because of the small variations in the high pressures due to the gas valve-handling operations and small variations in temperature of the measuring system, leading to significant errors in the number of hydrogen moles absorbed or desorbed.

The solubilities of hydrogen and deuterium in Pd at atomic ratios higher than about  $[\text{H}]/[\text{Pd}] = 0.6$  and about  $[\text{D}]/[\text{Pd}] = 0.65$  have been investigated in the temperature range from 195 to 373 K and at pressures from about  $1 \times 10^3$  Pa to 17 MPa [10, 12, 18–20]. The experimental results can be satisfactorily described by an equation relating the concentration of hydrogen (deuterium) in Pd and the fugacity of gaseous  $\text{H}_2(\text{D}_2)$ :

$$\log f_{\text{H}_2(\text{D}_2)} = -A(T) + B(T)[\text{H}][\text{D}]/[\text{Pd}] \quad (2)$$

where  $f_{\text{H}_2(\text{D}_2)}$  denotes the fugacity given by  $f_{\text{H}_2(\text{D}_2)} = p_{\text{H}_2(\text{D}_2)}\gamma_{\text{H}_2(\text{D}_2)}$ ,  $p_{\text{H}_2(\text{D}_2)}$  is the pressure

of gaseous hydrogen or deuterium,  $\gamma_{H_2(D_2)}$  is the fugacity coefficient [21], A(T) and B(T) are temperature-dependent constants, and  $[H]([D])/[Pd]$  is the atomic ratio.

Figure 1 shows a comparison of experimental and calculated hydrogen solubility isotherms at 298 K [10, 11]. The open circles denote the solubility data of Tkacz and Baranowski [11] plotted against the pressure of gaseous hydrogen ( $\log p_{H_2}$ ), the open triangles the same solubility data against the corresponding fugacity ( $\log f_{H_2}$ ) [11], and the open squares the data calculated [10] by extrapolating the Wicke–Nernst isotherm (equation (2)) measured at up to about 0.1 MPa to higher pressures ( $\log p_{H_2}$ ).

It can be seen that, in order to reach the stoichiometric composition PdH at 298 K, a pressure of about 12.2 kbar is required, where the corresponding fugacity is about  $f_{H_2} = 10^7$  bar. Furthermore, it should be noted that the  $n_H/n_{Pd}$ -values calculated by extrapolating the Wicke–Nernst [10] data to higher pressures are in agreement with the experimentally determined values of Tkacz and Baranowski [11] in the range  $f_{H_2} = 10^{3.8}$ – $10^{4.5}$  bar, which are plotted against the corresponding fugacity, although Wicke and Nernst [10] employed pressure instead of fugacity.

In this study in order to avoid the difficulty of obtaining  $[H]([D])/[Pd]$ -values at higher pressures, it was assumed that the  $[H]([D])/[Pd]$ -values corresponding to the pressures  $p_{H_2(D_2)} \gtrsim 0.4$  MPa coincide with the values obtained by extrapolating the Wicke–Nernst [10]  $p$ - $c$  data, i.e. using equation (2), to higher pressures for both the Pd–H and the Pd–D systems. By measuring the initial and final equilibrium pressures during the absorption and desorption processes, the  $[H]([D])/[Pd]$ -values were calculated according to similar equations to equation (2) based on the Wicke–Nernst [10] data.

The reaction for the  $\alpha$ - and  $\beta$ -single-phase region on both systems was completed rather quickly, within about 10 min, but the time for the two cells to return to the same temperature was about 60–90 min, and in the two-phase region, especially at the  $(\alpha + \beta)$ - $\beta$ -phase boundary, the time was about 3–4 h.

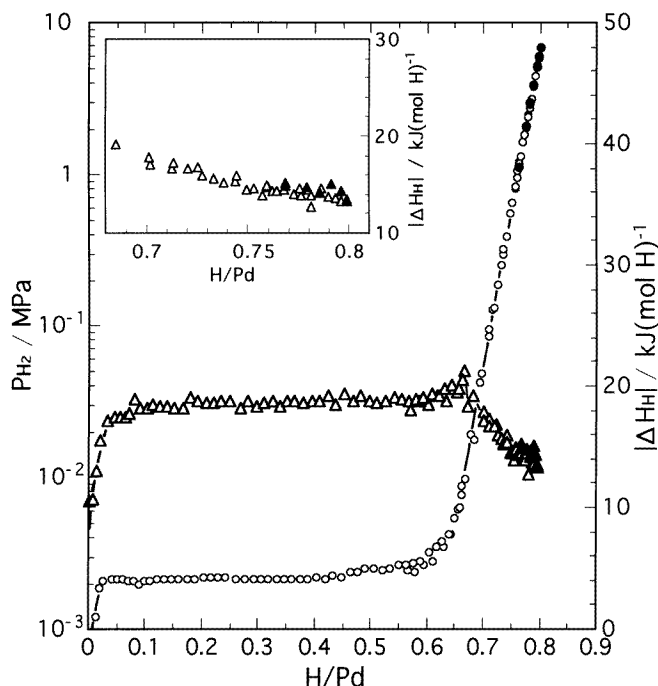
### 3. Results and discussion

#### 3.1. Calorimetric measurements at 298 K

The calorimetrically determined enthalpies as a function of  $[H]([D])/[Pd]$  for the Pd–H and Pd–D systems at 298 K are shown in figures 2 and 3, respectively, together with the measured  $p$ - $c$  isotherms, where open triangles represent the enthalpy of absorption, full triangles the enthalpy of desorption, open circles the corresponding  $H_2$  and  $D_2$  equilibrium pressures during absorption and full circles the pressures during desorption. The insets in the same figures are enlarged versions of the high-H(D)-concentration regions.

As has been observed previously [12, 22],  $\beta$ -hydride in the Pd–H system is more stable than that in the Pd–D system, because the  $\alpha + \beta$  two-phase plateau pressure for the Pd–H system is lower than that for the Pd–D system, and the high-pressure solubility in the Pd–H system is higher than that in the Pd–D system. The relationships between the enthalpies  $|\Delta H_{H(D)}|$  and  $[H]([D])/[Pd]$  have almost the same shapes for both the Pd–H system and the Pd–D system but, at the same H(D) content, the enthalpies  $|\Delta H_H|$  for the Pd–H system are somewhat higher than for the Pd–D system, i.e. more exothermic for the absorption processes.

In the  $\alpha$ -phase region, the values of  $\Delta H_{H(D)}$  for absorption become more exothermic with increasing H(D) content. For the  $\alpha + \beta$  two-phase region with  $[H]([D])/[Pd]$  of about 0.25–0.6, the  $\Delta H_{H(D)}$ -values are almost constant, independent of  $[H]([D])/[Pd]$  in both systems. The average values for absorption are  $\Delta H_H = -18.6 \pm 0.3$  kJ (mol H)<sup>-1</sup> and



**Figure 2.** Calorimetrically determined enthalpies  $|\Delta H_H|$  as a function of  $[H]/[Pd]$  for the Pd-H system at 298 K, together with the measured equilibrium pressures  $p_{H_2}$ :  $\Delta$ , enthalpy of absorption;  $\blacktriangle$ , enthalpy of desorption;  $\circ$ ,  $p_{H_2}$  for absorption;  $\bullet$ ,  $p_{H_2}$  for desorption.

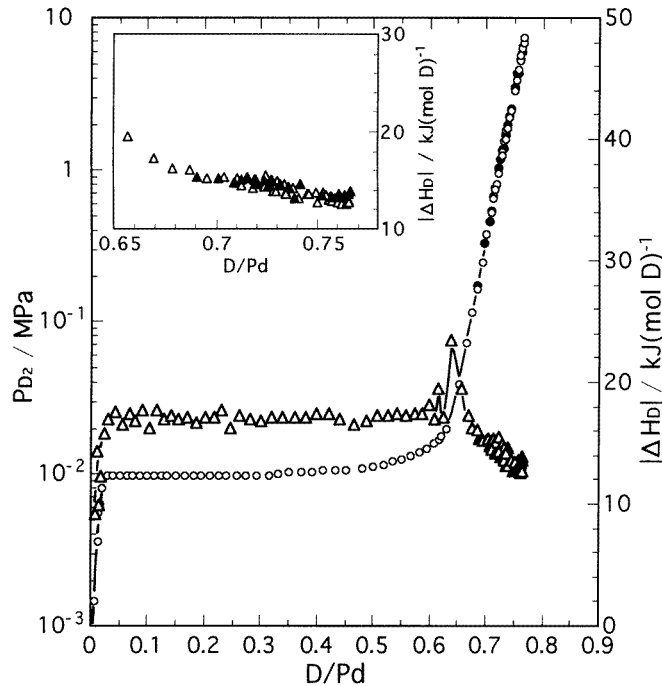
$\Delta H_D = -17.1 \pm 0.3 \text{ kJ (mol D)}^{-1}$ . These  $\Delta H_{H(D)}$ -values are in agreement with the previously reported values [12] and also with the values derived in the literature from van't Hoff plots of the two-phase plateau pressures [14].

At the  $(\alpha + \beta)$ - $\beta$  phase boundaries with  $[H]/[Pd] \simeq 0.66$  and  $[D]/[Pd] \simeq 0.64$ , a discontinuity in the enthalpies occurs owing to the compositional difference [12, 13], although at the  $\alpha$ - $(\alpha + \beta)$ -phase boundary the discontinuity in the enthalpy does not clearly appear. In the  $\beta$ -phase region, values of  $\Delta H_{H(D)}$  for absorption processes become less exothermic with increase in H(D) content, and there is no difference between the magnitudes of the enthalpies for absorption (open triangles) and desorption (full triangles). However, as mentioned above, at the same H(D) content the enthalpy values for the Pd-H system are slightly more exothermic than for the Pd-D system.

The relative partial molar entropy can be determined in the  $\alpha$ - and  $\beta$ -single-phase region using

$$\Delta S_{H(D)} = \Delta H_{H(D)}/T - R \ln p_{H_2(D_2)}^{1/2} \quad (3)$$

where  $\Delta H_{H(D)}$  is the calorimetrically determined values and  $p_{H_2(D_2)}$  is the equilibrium pressure, because there should be no hysteresis in the single-phase region. However, as has been discussed [12], for evaluation of the entropies for the  $\alpha + \beta$  two-phase region, neither  $p_f$  (plateau pressure of  $\beta$ -hydride formation) nor  $p_d$  (plateau pressure of  $\beta$ -hydride decomposition), instead of  $p_{eq} = (p_f p_d)^{1/2}$ , should be used for the respective plateau pressures, because there should be hysteresis in the two-phase region, although there is no difference between the magnitudes of the calorimetric enthalpies for hydride formation and



**Figure 3.** Calorimetrically determined enthalpies  $|\Delta H_D|$  as a function of  $[D]/[Pd]$  for the Pd-D system at 298 K, together with the measured equilibrium pressures  $p_{D_2}$ :  $\Delta$ , enthalpy of absorption  $\blacktriangle$ , enthalpy of desorption;  $\circ$ ,  $p_{D_2}$  for absorption;  $\bullet$ ,  $p_{D_2}$  for desorption.

decomposition [12].

In this study, nevertheless the entropies for the  $\alpha + \beta$  two-phase region were evaluated as a plateau formation entropy using the calorimetric enthalpies and the plateau pressure of  $\beta$ -hydride formation. The values of  $\Delta S_{H(D)}$  in the  $\alpha$ -phase region decrease steeply with increasing H(D) content. The entropy values for the  $\alpha + \beta$  two-phase region in both systems are nearly constant, independent of H(D) concentration. The average values for absorption are  $\Delta S_H = -46.2 \pm 0.5 \text{ J (mol H)}^{-1} \text{ K}^{-1}$  and  $\Delta S_D = -47.5 \pm 0.5 \text{ J (mol D)}^{-1} \text{ K}^{-1}$ . These  $\Delta S_{H(D)}$ -values are in agreement with the previously reported values determined in the literature from van't Hoff plots of the plateau pressures [14]. At the  $(\alpha + \beta)$ - $\beta$  phase boundaries, a discontinuity in the entropies also occurs, reflecting the discontinuity in enthalpies (figures 2 and 3). In the  $\beta$ -phase region, the  $\Delta S_{H(D)}$ -value for absorption in both systems tends to decrease gradually with increasing H(D) content in the range  $[H]/[Pd] > 0.73$  and  $[D]/[Pd] > 0.69$ , but there is no difference between the magnitudes of the entropies for absorption and desorption, and at the same H(D) contents there is also no marked difference between the magnitudes of the entropies of Pd-H and Pd-D systems.

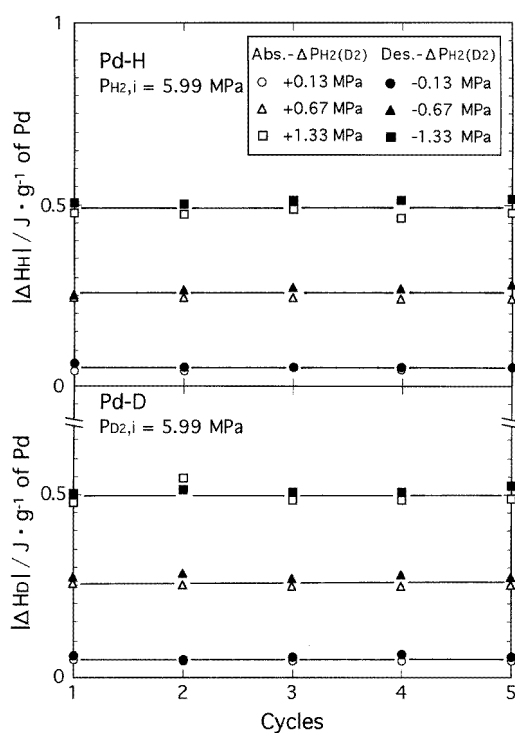
### 3.2. Effects of magnitude of cyclic absorption-desorption pressures at specified initial hydrogen (deuterium) gas pressures on the calorimetric enthalpies

In the previous 'cold-fusion' experiments [23-26,5], it was reported that a dynamic electrolysis method using a Pd cathode in heavy water and low-high-pulse current operation with several hours' repetition leads to anomalously large excess heats. The excess heat



generation during electrolysis seemed to occur by forming some enriched [D]/[Pd] ratio zone in the Pd cathode, leaving aside the question of the origin of the excess heat. Similar experiments in this study using a gas-phase method were carried out at 298 K by examining the effects of cyclic absorption–desorption pressures at specified initial pressures in the  $\beta$ -phase region on the calorimetric enthalpies for both systems.

Before the experiments, the initial equilibrium  $H_2$  and  $D_2$  pressures were regulated as follows:  $p_{H_2(D_2),i} = 0.67$  MPa, corresponding to initial H(D) contents of about  $[H]/[Pd] = 0.752$  and  $[D]/[Pd] = 0.714$ ;  $p_{H_2(D_2),i} = 2.67$  MPa which corresponds to about  $[H]/[Pd] = 0.782$  and  $[D]/[Pd] = 0.744$ ;  $p_{H_2(D_2),i} = 5.99$  MPa which corresponds to about  $[H]/[Pd] = 0.798$  and  $[D]/[Pd] = 0.761$ . At the respective initial pressures, by imposing cyclic absorption–desorption pressures of  $\Delta p_{H_2(D_2)}$  up to 5 cycles, the corresponding enthalpies for the cyclic hydride formation–decomposition were measured. The additional pressures of  $\Delta p_{H_2(D_2)}$  were selected as follows;  $\Delta p_{H_2(D_2)} = \pm 0.13$  MPa,  $\pm 0.67$  MPa and  $\pm 1.33$  MPa for the each initial pressure, where + indicates absorption and – indicates desorption.



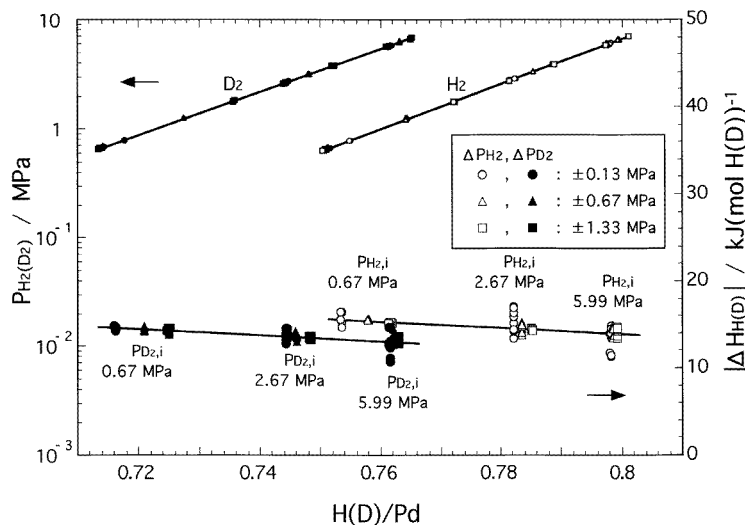
**Figure 4.** Calorimetrically determined enthalpies  $|\Delta H_{H(D)}|$  at 298 K in the Pd–H and Pd–D systems for experiments on the effects of the magnitude of cyclic absorption–desorption pressures  $\pm \Delta p_{H_2(D_2)}$  up to 5 cycles at an initial pressure  $p_{H_2(D_2),i} = 5.99$  MPa on the calorimetric enthalpies. The upper data are for the Pd–H system, and the lower data for the Pd–D system. The open symbols are for absorption, and the full symbols for desorption.

Figure 4 shows a typical result of the effect of cyclic absorption (Abs.)–desorption (Des.) with  $\Delta p_{H_2(D_2)}$  pressures up to 5 cycles at an initial equilibrium pressure of  $p_{H_2(D_2),i} = 5.99$  MPa on the calorimetric enthalpies in the Pd–H and Pd–D systems. The enthalpy values  $|\Delta H_{H(D)}|$  obtained are expressed in joules per gram of Pd. It can be seen

that values of  $|\Delta H_{H(D)}|$  for hydride formation and hydride decomposition in both systems do not change with the cyclic absorption-desorption up to 5 cycles, and that the  $|\Delta H_{H(D)}|$  values increase almost proportionally with increase in  $|\Delta p_{H_2(D_2)}|$ , although the  $|\Delta H_{H(D)}|$ -values for hydride decomposition with higher  $|\Delta p_{H_2(D_2)}|$  pressures are slightly larger.

The reason for the difference between the  $|\Delta H_{H(D)}|$ -values for hydride formation and hydride decomposition in the case of the experiments with higher  $\Delta p_{H_2(D_2)}$  pressures of  $\pm 0.67$  and  $\pm 1.33$  MPa is not known. However, in the experiments with higher  $\pm \Delta p_{H_2(D_2)}$ -values at initial high pressures  $p_{H_2(D_2),i}$ , e.g. in the cases of absorption processes when the reaction valve for  $H_2$  and  $D_2$  gas absorption (introduction) was opened, there was an instantaneous heat flux from the reference vessel towards the sample vessel, and then immediately the heat flux due to the hydriding, i.e. the heat of solution, occurred. Conversely, on opening the reaction valve for the gas desorption (removal), a heat flux from the sample vessel relative to the reference vessel occurred instantly, quickly following the heat flux due to the dehydriding.

As will be described later, these phenomena were pronounced for lower-temperature calorimetries with initially high equilibrium pressures. The origin of the instantaneous heat flux generation on opening the reaction valve for absorption or desorption is unknown; however, it may be associated with the differences between the heat conductivities and/or specific heats of the sample vessel containing Pd and Cu foil samples and the reference vessel containing only Cu foils, i.e. with the difference between the heat transfer effects in both the vessels from the gas reservoir which is not at the calorimeter temperature.



**Figure 5.** Calorimetrically determined enthalpies  $|\Delta H_{H(D)}|$  at 298 K as a function of  $[H]([D])/[Pd]$  in the Pd-H and Pd-D systems for experiments on the effects of the magnitude of cyclic absorption-desorption pressures  $\pm \Delta p_{H_2(D_2)}$  up to 5 cycles at initial pressures  $p_{H_2(D_2),i} = 0.67$ – $5.99$  MPa on the calorimetric enthalpies. The open symbols are for the Pd-H system, and the full symbols for the Pd-D system. The measured equilibrium pressures  $p_{H_2(D_2)}$  are shown in the upper part.

Figure 5 shows plots of the  $|\Delta H_{H(D)}|$ -values versus  $[H]([D])/[Pd]$  obtained in the experiments on the effect of cyclic absorption-desorption with the  $|\Delta p_{H_2(D_2)}|$  pressures up to 5 cycles at the specified initial equilibrium pressures  $p_{H_2(D_2),i}$  on the calorimetric

enthalpies in both systems. The  $|\Delta H_{H(D)}|$ -values decrease almost linearly with increasing  $[H]([D])/[Pd]$  and these results for the Pd–H and Pd–D systems fall on the plots shown in the insets of figures 2 and 3, respectively. It can be seen that the calorimetric enthalpies do not depend on the magnitudes of cyclic absorption–desorption pressures even at such initial high pressures in the  $\beta$ -phase region, and that there is no marked difference between the magnitudes of the enthalpies for absorption and desorption.

Thus, the present enthalpy data determined calorimetrically by the gas-phase method do not seem to offer support for the occurrence of any heat production in the Pd–D system which was previously observed during dynamic electrolysis with low–high-pulse current operation with several hours' repetition [23–26, 5].

### 3.3. Calorimetric enthalpies for hydrogen (deuterium) absorption in the $\beta$ -phase region at low temperatures down to 194.5 K

In order to examine calorimetric enthalpies for hydrogen (deuterium) solution in the  $\beta$ -phase, the calorimetry was extended to lower temperatures. The temperatures selected were 273, 239.2 and 223 K for the Pd–H system, and 273, 243, 223 and 194.5 K for the Pd–D system. The reason for the selection of these temperatures is because the previously determined  $p$ – $c$  isotherm data exist [10] for both systems at the temperatures for evaluating the H and D concentrations by measuring the initial and final equilibrium pressures in the absorption processes.

The low-temperature calorimetric measurements with higher  $p_{H_2(D_2)}$  pressures were generally difficult, in particular below 223 K, because as described above, when the reaction valve for  $H_2(D_2)$  absorption (introduction) was opened, an instantaneous heat flux was produced from the reference vessel towards the sample vessel before the occurrence of heat flux due to the heat of solution. Conversely, on opening the valve for  $H_2(D_2)$  gas desorption (removal), a heat flux in the opposite direction is instantly produced. Therefore, these phenomena lead more or less to the errors in enthalpy values derived from the integration of the heat flux versus time curves.

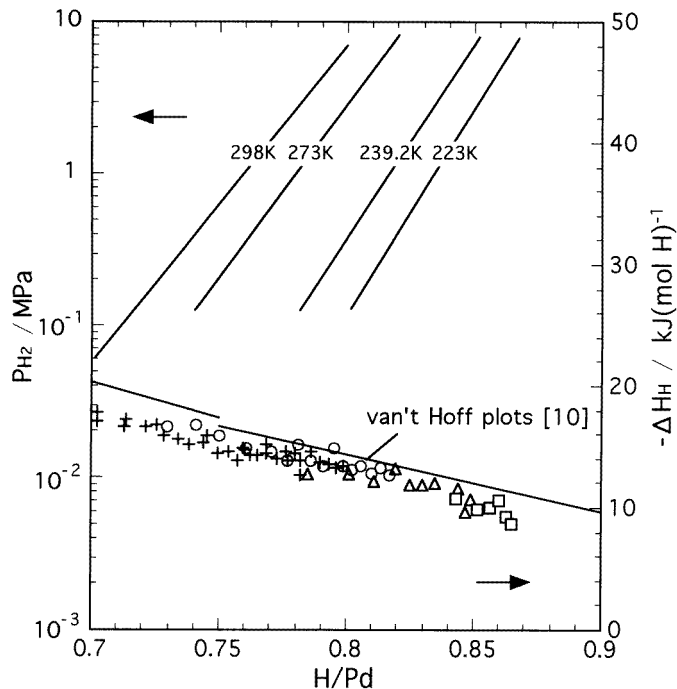
Figures 6 and 7 show the calorimetrically determined enthalpies for hydride and deuteride formations at the low temperatures for the Pd–H and Pd–D systems, respectively, together with data points for absorption at 298 K and with calculated enthalpies from van't Hoff plots by using the Wicke–Nernst [10] relative chemical potential. In the same figures, the  $p$ – $c$  isotherm data at each temperature [10] are also shown. For calculation of the enthalpies from van't Hoff plots [10], in the H(D) concentration region with  $[H]([D])/[Pd] < 0.75$ , the relative chemical potentials at 298 K, 273 K, 239.2 K (for the Pd–H system) and 243 K (for the Pd–D system) were used, and in the higher-concentration range, i.e. for  $[H]([D])/[Pd] > 0.75$ , the chemical potentials at 273 K, 239.2 K (for the Pd–H system), 243 K (for the Pd–D system), 223 K and 194.5 K were used.

It can be seen that the calorimetrically determined enthalpies for hydrogen and deuterium absorptions in the  $\beta$ -phase region become less exothermic almost linearly with increasing H and D content, independently of temperature, and that the linearly decreasing tendencies for both systems are in agreement with the calculated values from van't Hoff plots [10]. The dependence of the present calorimetric enthalpies on H and D concentrations in the range  $0.70 < [H]/[Pd] < 0.86$  and  $0.70 < [D]/[Pd] < 0.85$  is expressed as

$$\Delta H_H \text{ (kJ (mol H)}^{-1}) = 46.71[H]/[Pd] - 50.38 \quad (4)$$

and

$$\Delta H_D \text{ (kJ (mol D)}^{-1}) = 49.69[D]/[Pd] - 50.75. \quad (5)$$

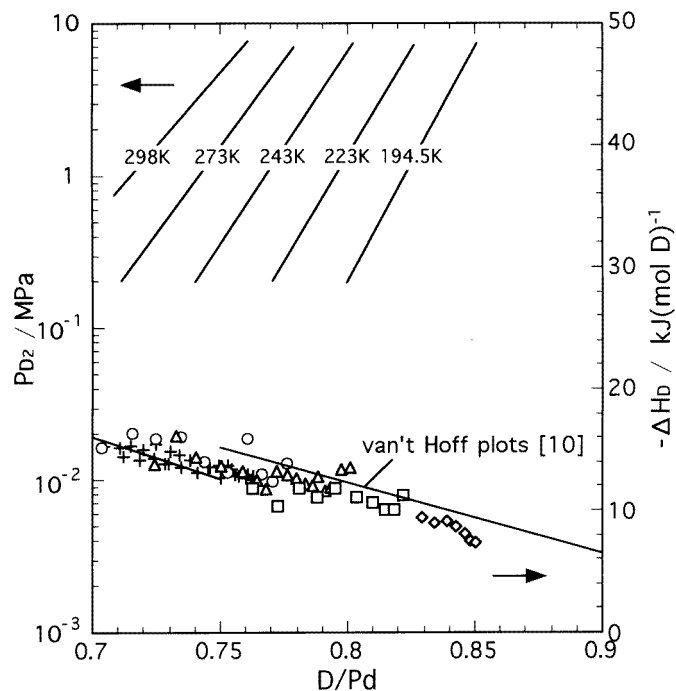


**Figure 6.** Calorimetric enthalpies  $-\Delta H_H$  as a function of hydrogen content with  $[H]/[Pd] > 0.7$  for absorption at different temperatures in the Pd-H system, together with values determined from van't Hoff plots [10]: +, 298 K; o, 273 K;  $\Delta$ , 239.2 K;  $\square$ , 223 K. The  $p_{H_2}$ - $[H]/[Pd]$  isotherms at each temperature [10] are shown in the upper part.

At the same H(D) content, the enthalpies for the Pd-H system are a little more exothermic than for the Pd-D system.

The corresponding entropies were also calculated from the relation  $\Delta S_{H(D)} = \Delta H_{H(D)}/T - R \ln p_{H_2(D_2)}^{1/2}$  for the Pd-H and Pd-D systems. There is scatter in the entropy values; however, it can be seen that the entropies for H and D absorptions have a tendency to decrease gradually with increasing H(D) content independently of temperature; however, there is no marked difference between the magnitudes of the  $\Delta S_{H(D)}$ -values for the two systems.

The relative contributions of the excess enthalpy  $H_H^E$  and excess entropy  $S_H^E$  to the partial excess chemical potential of hydrogen have been obtained [13] by assuming that the  $H_H^E$ - and  $S_H^E$ -values are temperature independent in the range 250–650 K, although there is considerable disagreement concerning values and trends of  $H_H^E$  and  $S_H^E$  in the high-H-content  $\beta$ -phase region [10, 12, 13, 27]. However, the interesting feature of the previous data [12, 13] is that the non-ideal configurational entropy  $S_H^E$  changes sign from negative to positive at about  $[H]/[Pd] = 0.65$ , although it should be noted that the positive and negative contributions to the excess configurational entropies must balance:  $\int_0^1 S_H^{E,c} dr = 0$ . This change in sign means that, below  $[H]/[Pd] = 0.65$ , there is a tendency for some ordering of the hydrogen atoms to occur and, above 0.65, the ordering starts to break down. For the Pd-D system a change in the sign of the excess entropy was also observed [12].



**Figure 7.** Calorimetric enthalpies  $-\Delta H_D$  as a function of deuterium content with  $[D]/[Pd] > 0.7$  for absorption at different temperatures in the Pd–D system, together with the values determined from van't Hoff plots [10]: +, 298 K; O, 273 K; Δ, 243 K; □, 223 K; ◇, 194.5 K. The  $p_{D_2}$ – $[D]/[Pd]$  isotherms at each temperature [10] are shown in the upper part.

The excess chemical potential  $\mu_{H(D)}^E$  of hydrogen and deuterium is defined by

$$\mu_{H(D)}^E = RT \ln p_{H_2(D_2)}^{1/2} - \Delta\mu_{H(D)}^0 - RT \ln[r/(1-r)] \quad (6)$$

where  $r$  is the  $[H]/[Pd]$  or  $[D]/[Pd]$  ratio and  $\Delta\mu_{H(D)}^0$  is the relative chemical potential at infinite dilution. The partial excess enthalpy  $H_{H(D)}^E$  and partial excess entropy  $S_{H(D)}^E$ , which is the non-ideal partial entropy, can be calculated, respectively, from the relations

$$H_{H(D)}^E = \Delta H_{H(D)} - \Delta H_{H(D)}^0 \quad (7)$$

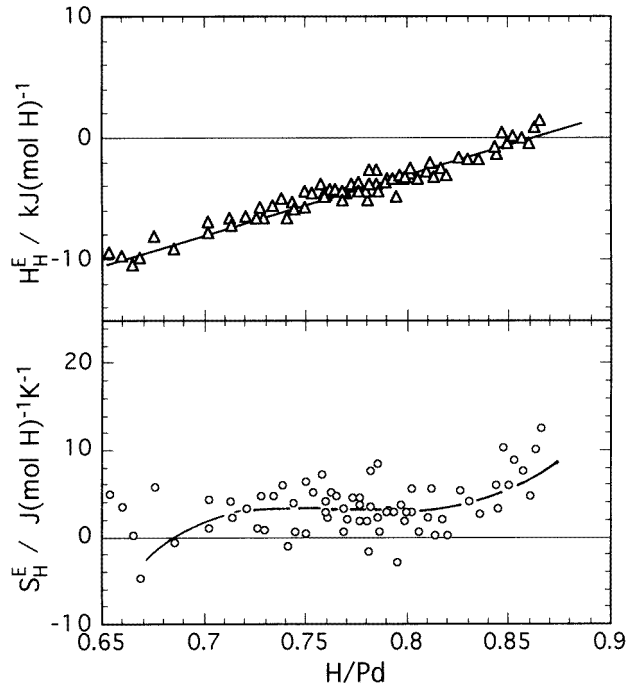
and

$$S_{H(D)}^E = \Delta H_{H(D)}/T - \Delta S_{H(D)}^0 + R \ln[r/(1-r)] - R \ln p_{H_2(D_2)}^{1/2} \quad (8)$$

where  $\Delta H_{H(D)}^0$  and  $\Delta S_{H(D)}^0$  are the relative partial molar enthalpy and relative partial molar entropy, respectively, at infinite dilution.

In the present study, in order to examine the dependences of  $H_{H(D)}^E$ - and  $S_{H(D)}^E$ -values on H(D) content in the ranges  $[H]/[Pd] > 0.68$  and  $[D]/[Pd] > 0.65$ , according to equation (7) and (8), the following  $\Delta H_{H(D)}^0$ - and  $\Delta S_{H(D)}^0$ -values were taken:  $\Delta H_H^0 = -10.1 \text{ kJ (mol H)}^{-1}$  [28],  $\Delta S_H^0 = -53.7 \text{ J (mol H)}^{-1} \text{ K}^{-1}$  [28],  $\Delta H_D^0 = -8.47 \text{ kJ (mol D)}^{-1}$  [29] and  $\Delta S_D^0 = -55.2 \text{ J (mol D)}^{-1} \text{ K}^{-1}$  [29].

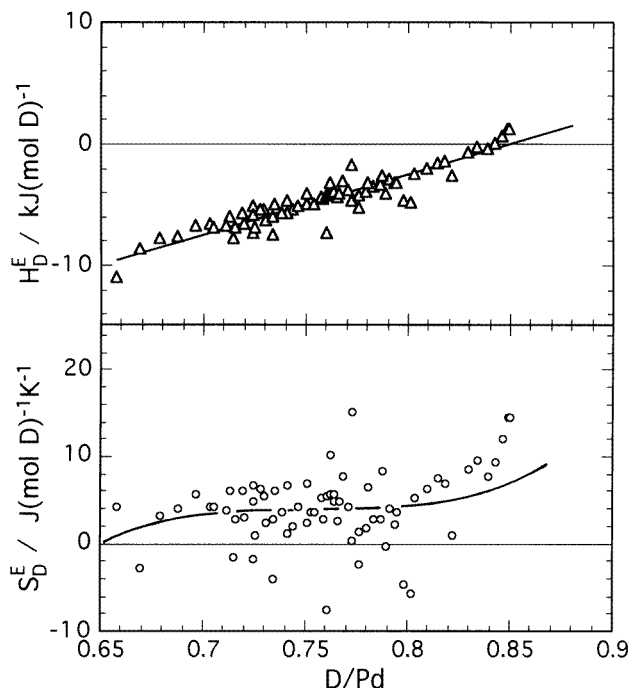
Figures 8 and 9 show plots of the derived  $H_{H(D)}^E$ - and  $S_{H(D)}^E$ -values as functions of  $[H]([D])/[Pd]$  in the Pd–H and Pd–D systems, respectively, where the data points are



**Figure 8.** Plots of the partial excess enthalpy  $H_H^E$  ( $\Delta$ ) and partial excess entropy  $S_H^E$  ( $\circ$ ) for hydrogen absorption in Pd as functions of hydrogen content with  $[H]/[Pd] > 0.68$  in the temperature range 298–223 K. The  $H_H^E$ - and  $S_H^E$ -values at the respective temperatures were calculated from equations (7) and (8), respectively, together with equation (4), and are shown as open circles for  $S_H^E$  and as open triangles for  $H_H^E$ , by assuming that the  $\Delta H_H$ -values are independent of temperature over the range studied. The solid line and curve in the  $H_H^E$ - $[H]/[Pd]$  and  $S_H^E$ - $[H]/[Pd]$  plots, respectively, are the average values of the experimental temperatures.

expressed as open circles for  $S_{H(D)}^E$  and open triangles for  $H_{H(D)}^E$ , by assuming that the  $\Delta H_{H(D)}$ - and  $\Delta S_{H(D)}$ -values are independent of temperature over the range studied, 298–194.5 K, although all the values were, of course, calculated at the respective temperatures. The solid lines in the plots of  $H_{H(D)}^E$  versus  $[H]([D])/[Pd]$  and the solid curves in the plots of  $S_{H(D)}^E$  versus  $[H]([D])/[Pd]$  are the average values of the experimental temperatures.

It can be seen from the partial excess enthalpy data that the attractive interaction enthalpies of dissolved hydrogen (deuterium) in Pd decrease linearly with increase in H(D) content and become zero at about  $[H]/[Pd] = 0.86$  and  $[D]/[Pd] = 0.845$  for the Pd–H and Pd–D systems, respectively, and thus in the much-higher H(D)-content region the occurrence of repulsive interaction enthalpies can be inferred. As for the  $S_{H(D)}^E$ -values, after changing sign from negative to positive at about  $[H]/[Pd] = 0.69$  and  $[D]/[Pd] = 0.65$  for the Pd–H and Pd–D systems, respectively, the  $S_{H(D)}^E$ -values seem to remain almost constant at  $3 \pm 1.5 \text{ J (mol H(D))}^{-1} \text{ K}^{-1}$  for  $[H]/[Pd]$  up to about 0.82 and for  $[D]/[Pd]$  up to about 0.80; then the positive  $S_{H(D)}^E$ -values have a tendency to increase gradually with increasing H(D) content. Therefore, it can be inferred that in the high-H and high-D content regions the ordering of H and D atoms in Pd, discussed with respect to the  $S_{H(D)}^E$ -values with  $[H]/[Pd] \lesssim 0.69$  and  $[D]/[Pd] \lesssim 0.65$ , is breaking down.



**Figure 9.** Plots of the partial excess enthalpy  $H_D^E$  ( $\Delta$ ) and partial excess entropy  $S_D^E$  ( $\circ$ ) for deuterium absorption in Pd as functions of deuterium content with  $[D]/[Pd] > 0.65$  in the temperature range 298–194.5 K. The  $H_D^E$ - and  $S_D^E$ -values at the respective temperatures were calculated from equations (7) and (8), respectively, together with equation (5), and are shown as open circles for  $S_D^E$  and as open triangles for  $H_D^E$ , by assuming that the  $\Delta H_D$ -values are independent of temperature over the range studied. The solid line and curve in the  $H_D^E$ - $[D]/[Pd]$  and  $S_D^E$ - $[D]/[Pd]$  plots, respectively, are the average values of the experimental temperatures.

#### 4. Conclusions

The calorimetrically determined relative partial molar enthalpies  $\Delta H_{H(D)}$  and entropies  $\Delta S_{H(D)}$  of absorption of hydrogen and deuterium at  $[H]([D])/[Pd] = 0.7$ – $0.86$  in the  $\beta$ -phase region of the Pd–H and Pd–D systems are almost independent of temperature over the range 194.5–298 K. The  $\Delta H_{H(D)}$ -values becomes less exothermic in an almost linear fashion with increasing H or D content. At the same H(D) concentration, the enthalpy values for the Pd–H system are slightly more exothermic than for the Pd–D system. The results are in agreement with the enthalpies derived from van't Hoff plots using the Wicke–Nernst relative chemical potential. The  $\Delta S_{H(D)}$ -values have a tendency to decrease gradually with increase in H(D) content; however, there is no marked difference between the magnitudes of the relative partial molar entropies of the Pd–H and Pd–D systems. The calorimetric enthalpies measured at 298 K in the  $\beta$ -phase region of both systems nearly do not depend on the magnitude of the cyclic imposed absorption-desorption pressures with  $\Delta p_{H_2(D_2)}$  from  $\pm 0.133$  to  $\pm 1.33$  MPa at specified initial equilibrium pressures  $p_{H_2(D_2),i}$  from 0.67 to 5.99 MPa, and there is no marked difference between the magnitudes of the relative partial molar enthalpies for absorption and desorption. The present calorimetric enthalpy data do not offer support for the occurrence of any heat production even at  $[D]/[Pd] \simeq 0.85$  in the

Pd–D system, because the enthalpies determined calorimetrically and from van't Hoff plots agree.

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