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Solubility of hydrogen isotopes in palladium

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An all-metal facility has been built to handle about 1000 Ci of tritium for studies of the tritium behavior in metals. First measurements of the pressure-composition-temperature relationship for the palladium-tritium system PdT_x are reported for the pressure range $0.1 \leq p \leq 2$ bar, the composition range $0.02 \leq x \leq 0.65$, and the temperature range $35 \leq T \leq 125\,^{\circ}C$ together with the results of the PdH and PdD systems measured under the same experimental conditions. The main conclusions are that the inequality $p_{T_2} > p_{D_2} > p_{H_2}$ holds at equal concentrations and temperatures and that the $\beta \rightarrow \alpha$ transition enthalpies show a strong isotopic effect, whereas the entropies do not.

I. INTRODUCTION

The palladium-hydrogen system has been the most extensively studied metal-hydrogen system and still attracts great attention as demonstrated by numerous review articles.[1-3] The first publication appeared as early as 1866.[4] Following the discovery of deuterium,[5] the palladium-deuterium system[6] has been investigated since 1935. Since tritium is now available in large quantities at a reasonable cost and high purity, some papers have appeared on the properties of tritium in metals. To our knowledge only one paper[7] dealing with the PdT_x system has appeared thus far where the solubility of tritium only in the very dilute α phase ($x \leq 0.015$) is discussed.

In this paper we will present the first measurements of PdT_x in the concentration (x) range ($0.02 \leq x \leq 0.65$), pressure (p) range ($0.1 \leq p \leq 2$ bar), and temperature (T) range ($35 \leq T \leq 125\,^{\circ}C$). The results will be compared with the data for protium and deuterium using the same sample under identical experimental conditions. Furthermore, the details of the apparatus and the precautions employed to ensure safe handling of the 1000-Ci tritium will be discussed shortly.

The three isotopes H, D, and T have the largest relative mass changes of all isotopic species and are therefore expected to exhibit large isotope effects. They are based mainly on the mass dependence of the vibrational energy levels of the hydrogen atoms in the lattice and the rotational and vibrational levels of the molecules in the gas. Those investigations of all three hydrogen isotopes constitute a valuable test for theories. Furthermore, the knowledge of the behavior of tritium in metals is of importance for its possible application in future fusion reactors and for the safe storage of large tritium amounts as metal tritides.

Pd is especially suited for the present investigations, since it easily absorbs hydrogen due to the removal of oxide surface layers in a hydrogen atmosphere, which in turn results in catalytically active sites that are necessary for the splitting of the H_2 molecules and the recombination of H atoms.

II. Experimental Procedure

A. Apparatus

An all-metal ultrahigh-vacuum (UHV) apparatus has been constructed for the loading of metal samples with tritium and the stable hydrogen isotopes up to high concentrations, degassing the metal tritide samples, and measuring the pressure, composition, and temperature relationship of different metal-hydrogen systems. The equipment is similar to those[8,9] which have been employed for the stable hydrogen isotopes, but because of the radiation hazards associated with the handling of 1000 Ci of tritium some important modifications were made to assure safe operation.

Secondary containment has been used in the construction of the loading apparatus. Hot walls in contact with high tritium pressures are surrounded by double-walled steel cylinders in order to capture the tritium which has permeated the hot walls.

The entire apparatus is placed in a ventilated hood and the exhaust air from the hood is continuously monitored with a tritium monitor. Additionally, the air in the laboratory is ventilated so that a directional air stream is generated and controlled by a second tritium monitor. No increase in the count rate of the monitors by heating the UT_x storage containers or the sample chamber could be detected.

Only a small increase of tritium inside the hood was observed during the opening of the sample chamber due to the desorption of tritium from the inside chamber walls. Opening is necessary to remove samples for other types of measurements, such as diffusion,[10] lattice parameter,[11] differential thermoanalysis,[12] and evolution[13] measurements, etc.

Two tritium sources are included in the system—a 1000-Ci source purchased from Nukem Ltd. and a 100-Ci source of our own design shown in Fig. 1. By heating the oven (4) the tritium is evolved from the uranium powder (1) to the desired pressure. During the cooling phase the uranium absorbs the T_2 gas very rapidly. The T_2 equilibrium pressure over the UT_x in the two-phase region is about 4×10^{-5} mbar (Ref. 14) at room temperature. Owing to tritium decay there is always ^3He gas in the system after heating of the tritium source. This gas is evacuated by an ion-getter pump.

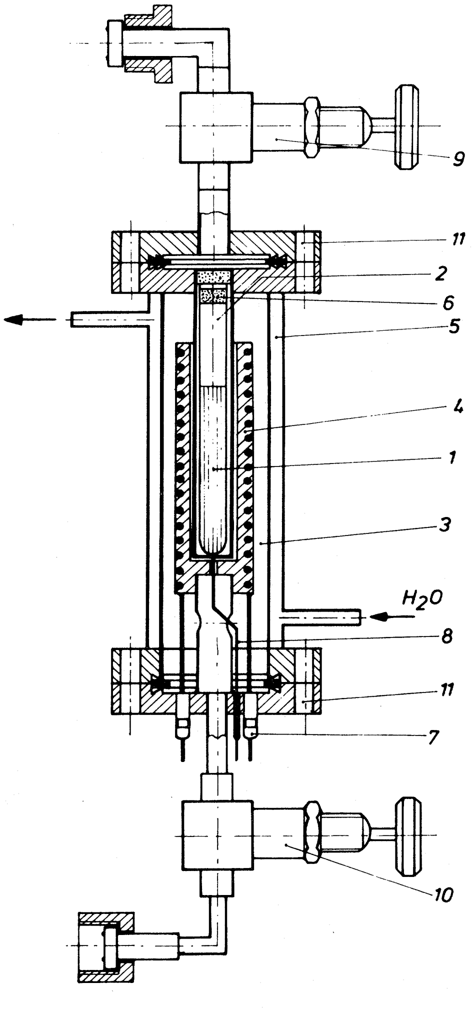

FIG. 1. Cross section of the 100-Ci UT_x storage container. (1, UT_x powder; 2, T_2-filled cylinder; 3, Ar-filled volume; 4, oven with Mo winding; 5, water-cooled volume; 6, filter; 7, current feed throughs; 8, thermocouple; 9, valve for closing the T_2-filled cylinder; 10, valve for closing the Ar-filled volume; 11, CF-35 flanges.)

During heating, the stainless-steel wall of the inner cylinder also gets hot, and a greater permeation of tritium into the argon-filled space (3) can be expected. The tritium which has permeated the hot wall is caught in volume (3) which is surrounded by water-cooled stainless-steel walls. No T_2, HTO, or T_2O molecules have been detected by mass spectroscopy upon analysis of the gas in the volume (3), which indicates that the permeation is probably strongly reduced by oxide layers on the surfaces.

A cross section of the sample chamber to prepare the metal tritides is shown in Fig. 2. The oven (1) is built inside of the chamber so that the walls can be cooled by circulating water (2) to reduce the permeation of tritium. Any tritium which has permeated may be captured in the water. The current feed throughs (4) are protected with a vacuum-sealed hood (5) to prevent any tritium release in case of a break in one of the current feed throughs. Shielded thermocouples (6) are used to regulate the oven temperature and to measure the sample temperature.

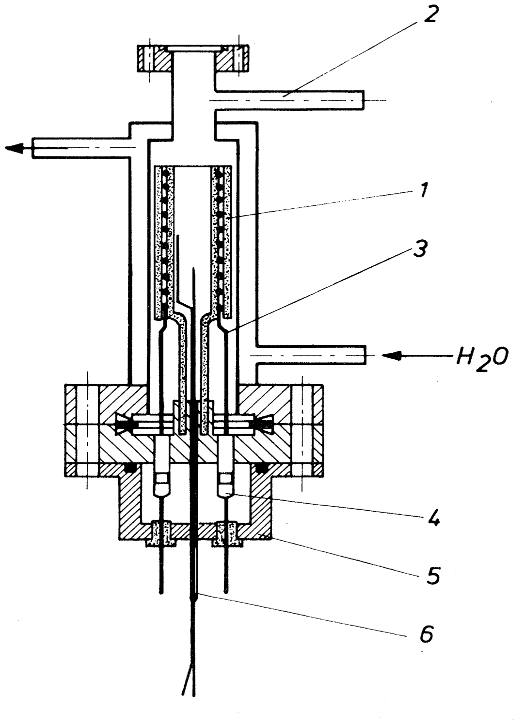

FIG. 2. Cross section of the sample chamber for the preparation of metal tritides. (1, oven made of quartz; 2, T_2-filled volume; 3, Mo winding; 4, thermocouple; 5, vacuum-sealed hood; 6, shielded thermocouples.)

For the determination of the correct pressures of the T_2 gas with capacitance manometer sensors, it is essential to avoid the use of heads of the double-sided version with the prestressed diaphragm welded between two fixed electrodes. If the dielectric constant of the measured gas is constant, the output voltage is directly proportional to the applied pressure. This is no longer true in the case where the dielectric constant of the gas differs significantly from unity as for radioactive gases. Therefore, single-sided capacitance sensors have to be used with both electrodes on one side of the pressure transducer which is always surrounded by the same rest-gas compositions. In order to show the deviations of the pressure readings obtained with capacitance manometer sensors of the single- and double-sided versions for ^{4}He and T_2 gas in an expanded way, the relative differences between these pressures are plotted in Fig. 3 as a function of the pressure obtained by the single-sided version. In the case of ^{4}He the pressures measured with the different sensors agree very well, illustrating the equality of both types of heads for nonradioactive gases. Furthermore, below about 50-mbar pressure both types of instruments function equally for the measurement of ^{4}He and T_2 gas. However, from about 50 mbar up to 1 bar T_2 pressure, the error in the pressure measurement of the double-sided version increases up to about 12% for the radioactive gas due to the additional current generated by the decay of the tritium atoms. The reason for the relatively large error of about 0.3% for He and T_2 gas in the low-pressure range is that a 10^3 and 10^4 Torr sensor head of different producers was used and showed different electronic drifts of the zero points. These measurements were done with ^{4}He instead of H_2 and D_2 to avoid loss of the purity of the T_2 gas by stable hydrogen isotopes. In addition, the relative differnce between the dielectric constants of ^{4}He and H_2 gas is only about $2\times10^{-2}\%$.[15]

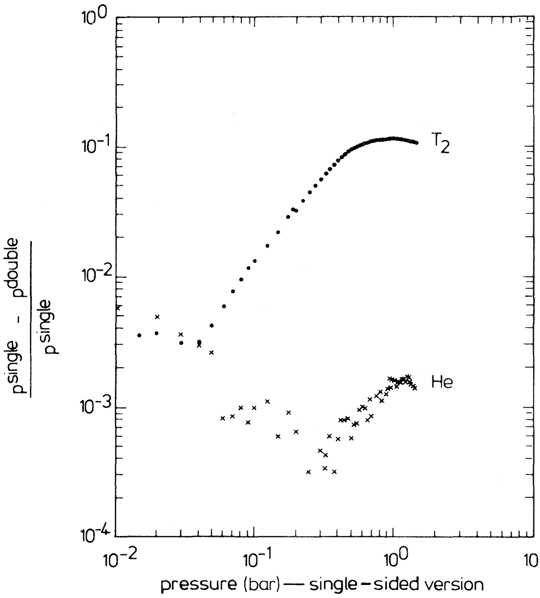

FIG. 3. Relative difference between the pressures of ^{4}He and T_2 gases measured with capacitance manometers of the single- and double-sided versions as a function of the pressure obtained by the single-sided sensor head.

B. Materials

Palladium (99.99% purity) was purchased from Heraeus GmbH Hanau. The main impurities are 20-ppm Fe, 20-ppm Ca, and 20-ppm Mg as detected by emission spectroscopy.

Before the experiments, Pd foil, 10 μm thick, was degassed in a UHV apparatus at 800 °C and 10^{-9} mbar. The foil was wound around the inner thermocouple (Fig. 2) to achieve correct temperature data.

For the isotopic studies the purity of the H_2 gas used was better than 99.9999 vol %. The D_2 gas was about 99.7% pure with most of the residual 0.3% being H_2. Both isotopes were obtained from FeTi-hydrogen storage containers.[16] The purity of the T_2 gas employed was 95.2 at. % T, 3.7 at. % H, and 1.1 at. % D.

No corrections for the measured tritium equilibrium pressures due to the slightly impure T_2 gas will be made in the following. Furthermore, the influence of the ^{3}He atoms generated by the tritium decay in the gas and in the metal will be neglected. This seems to be justified because the inert ^{3}He has been always removed from the T_2 gas after a few measurement cycles. The maximum activity in the present measurements was 215 Ci in the β phase of PdT_x.

After longer measurement periods with high tritium pressure, and subsequent absorption of the tritium in a cold uranium bed, some CT_4 was detected by mass spectrometry in the residual ^{3}He gas. The CT_4 molecules could be due to isotope exchange of oil vapor and cracking of the oil, and/or reaction of the tritium with carbon in the stainless steel.

C. Procedure

The experiments were carried out separately for each hydrogen isotope in the sequence PdH_x, PdD_x, and PdT_x. Before each new hydrogen isotope, the sample and the equipment were degassed for a long period to avoid isotopic exchange.

The H, D, or T concentration in the sample can be calculated from measurements of the pressure changes and the room and sample temperature, using the sample mass, system volume, and the effective temperature of the gas. This calculation was performed by a PDP 11 computer, which measured these quantities and controlled the sample temperature. Measurements were made at intervals of 5° or 10° always using the same volume.

A detailed description of the tritium loading apparatus, and of the special precautions to ensure safe handling of the 1000-Ci tritium and to measure the tritium-loaded samples outside the loading machine, as well as description of the computer system is given in Ref. 17.

III. RESULTS

Measurements of pressure, composition, and temperature yield the isotherms for the three isotopes shown in Figs. 4—8. The experimental data are represented by circles. The desorption data for the hydrogen isotopes are plotted in Figs. 4—6 and the absorption data in Figs. 7 and 8. A partial listing of the desorption data of PdT_x is given in Table I. In the case of PdT_x, the rate of tritium uptake was about a factor of 10 slower than that of the stable isotopes. Therefore, only the desorption isotherms of PdT_x were determined which can be taken as the equilibrium curves.[2] At the moment we do not understand the very slow tritium uptake. The desorption rate of tritium was similar to those observed for the PdH_x and PdD_x system and the T_2 gas used should be very pure due to the gettering properties of uranium. Furthermore, repeated measurements with hydrogen after termination of the tritium cycles showed no decrease of the hydrogen uptake rate, demonstrating that the Pd-sample surface was still active. The present data for PdH_x and PdD_x are in good agreement with those of other groups.[18–21] Therefore, we will mainly discuss the new PdT_x desorption data. A comparison of Figs. 4—6 demonstrate that the overall shape of the PdT_x isotherms—and therefore of the phase diagram of PdT_x—is very similar to those for PdD_x and PdH_x. Therefore, we will separate the isotherms of PdT_x into a dilute α-phase, a high concentrated β phase, and a two-phase region $\alpha+\beta$ as in the PdH and PdD phase diagrams, and discuss each region separately.

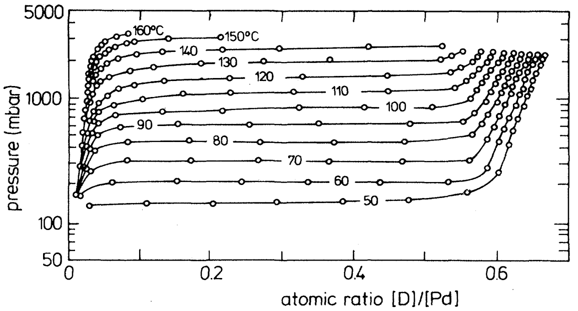

FIG. 5. Desorption isotherms of the system PdD_x.

A. α phase of PdT_x

Our experimental data of PdT_x up to $x=0.10$ which includes the α and some of the $\alpha+\beta$ phases are shown in Fig. 9. In addition, some results of Ref. 7 are plotted together with the 70 °C and 120 °C isotherms of PdT_x in the α phase using Sieverts's law. For the small concentrations $0.005 \leq x \leq 0.008$ the experimental points do not lie exactly on the plotted straight lines. This deviation is larger at higher concentrations and is a consequence of the attractive H-H interaction. Although we have not measured enough data in the dilute α phase to again determine the standard-desorption enthalpies and entropies of H, D, and T, our experimental results show that in the α phase the solubility of tritium is lower than that of deuterium and protium ($x_T < x_D < x_H$) at equal temperatures and pressures. The α phase of PdT_x covers concentrations up to about $x=0.025$ in the measured temperature range

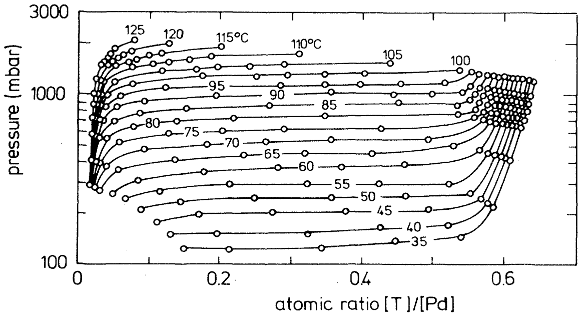

FIG. 4. Desorption isotherms of the system PdT_x.

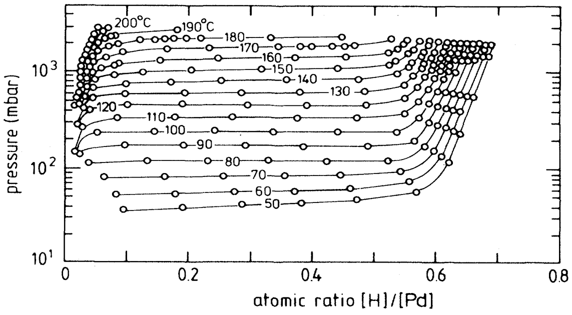

FIG. 6. Desorption isotherms of the system PdH_x.

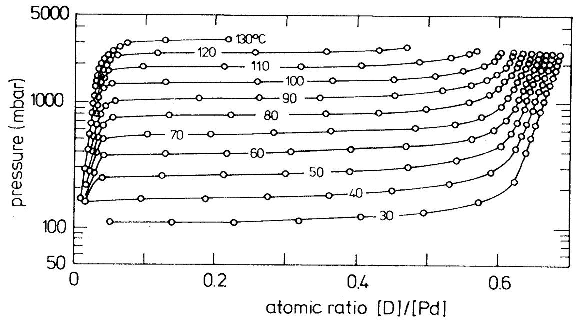

FIG. 7. Absorption isotherms of the system PdD_x.

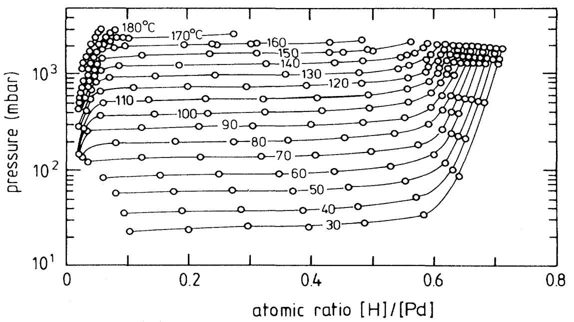

FIG. 8. Absorption isotherms of the system PdH_x.

and the phase boundary (solvus) between the α and $\alpha+\beta$ phases shows only a very weak temperature dependence.

B. $\alpha+\beta$ phase of PdT_x

After crossing the solvus β phase regions start to precipitate within the α phase. During the $(\alpha\rightarrow\beta)$ phase transformation, the hydrogen isotope pressure remains essentially constant (plateau pressure). The horizontal plateau pressures in Figs. 4—8 are characteristic of the coexistence of two solid phases with a gas phase.

The 70 °C, 80 °C, and 90 °C desorption isotherms of all three hydrogen isotopes are plotted in Fig. 10. A comparison of the pressures (p) of the hydrogen isotopes shows that in the two-phase region $p_{T_2} > p_{D_2} > p_{H_2}$ at equal temperatures, at all concentrations. All determined plateau pressures are listed in Table II. Furthermore, the desorption plateau pressures of tritium, deuterium, and protium are drawn in Fig. 11 as a function of reciprocal temperature. In the two-phase regions the pressure can be described by the equation

$$\ln(p/1\ \text{bar}) = -\frac{\Delta H^{\beta\rightarrow\alpha}}{RT} + \frac{\Delta S^{\beta\rightarrow\alpha}}{R}\ , \qquad (1)$$

where $\Delta H^{\beta\rightarrow\alpha}$ and $\Delta S^{\beta\rightarrow\alpha}$ represent the $\beta\rightarrow\alpha$ transition enthalpy and entropy, respectively, and R is the gas constant. Least-squares fits of the data in Table II yielded the values of the $\beta\rightarrow\alpha$ and $\alpha\rightarrow\beta$ transition enthalpies and entropies listed in Table III. The agreement with the results of other groups.[2,18] is satisfactory. Our values show a strong isotopic dependence for the transition enthalpies, but a negligible one for the transition entropies. In the two-phase region the decomposition pressure is always much lower than the formation pressure for a given temperature (see Table II). This is the well-known hysteresis effect of metal-hydrogen systems[22] in the absorption and desorption cycle.

C. β phase in PdT_x

After crossing the phase boundary between the $\alpha+\beta$ and β phases, a further increase of the hydro-

TABLE I. Desorption data [pressure (p), concentration (x) of different isotherms for the palladium tritium system].

40 °C		50 °C		60 °C		70 °C		80 °C	
p (mbar)	x (%)	p (mbar)	x (%)	p (mbar)	x (%)	p (mbar)	x (%)	p (mbar)	x (%)
147.7	13.1	205.6	8.9	262.3	4.9	284.6	2.5	292.4	2.0
150.3	19.6	231.2	14.5	314.4	8.5	378.8	3.9	398.1	2.6
149.0	32.3	250.4	24.9	350.8	17.7	467.8	9.3	544.1	3.9
163.0	42.6	252.6	35.6	366.6	28.1	506.5	18.1	650.6	7.9
168.5	52.1	251.2	46.1	378.5	37.0	526.5	26.4	702.3	13.9
229.8	57.7	264.9	55.2	390.5	46.0	534.3	35.7	729.0	21.9
420.7	60.2	443.5	58.6	475.1	56.4	547.5	49.3	751.1	34.8
656.4	61.7	676.6	60.4	699.4	58.9	727.0	57.0	779.2	53.4
728.3	62.4	747.5	61.2	769.1	59.8	794.1	58.2	827.7	55.9
813.9	62.7	833.6	61.4	854.2	60.1	879.1	58.5	909.8	56.5
901.4	62.9	920.2	61.7	941.4	60.4	964.3	58.9	992.8	57.1
998.4	63.1	1017.5	61.9	1038.2	60.6	1060.0	59.3	1087.1	57.6
1250.2	63.5	1268.4	62.4	1289.8	61.2	1311.2	59.9	1335.8	58.4

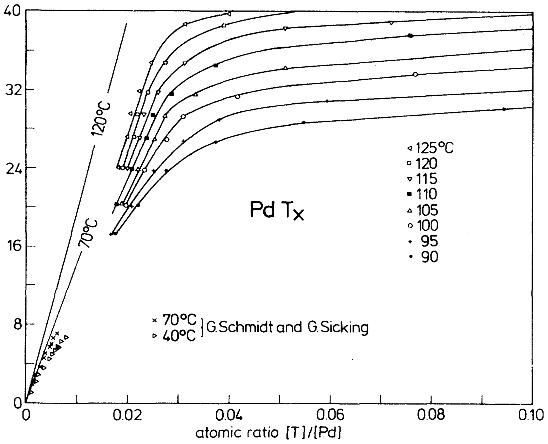

FIG. 9. Desorption isotherms of the system PdT_x ($x \leq 0.10$) with results of Ref. 7.

gen concentration is only achieved by relatively large pressure increases (see Figs. 4—8 and 10 for $x > 0.5$). The relationship between pressure and concentration in the β phase can be described by the phenomenological equation[18]

$$\ln(p_{T_2}/1\ \text{bar}) = -A(T) + B(T)x\ . \qquad (2)$$

The values for A and B are listed in Table IV together with the results of Ref. 18. They agree with Ref. 18 in the overlapping temperature range and show the same decrease with increasing temperature.

Table V lists the concentrations of the phase boundary between the $\alpha+\beta$ and β phase in the temperature range $50 \leq T \leq 130\,°C$ for all three hydrogen isotopes. The values were obtained from intersections of extrapolated pressures from the $\alpha+\beta$ phase and the β phase.

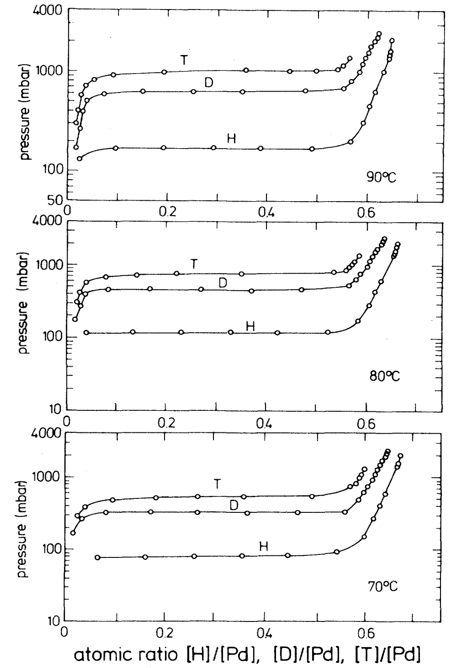

FIG. 10. 70 °C, 80 °C, and 90 °C desorption isotherms for the three hydrogen isotopes protium (H), deuterium (D), and tritium (T) in palladium.

IV. DISCUSSION

The main results of our experimental work concerning the solubilities of the three hydrogen isotopes in Pd can be formulated as follows: $x_T < x_D < x_H$ at equal pressures and temperatures and $p_{H_2} < p_{D_2} < p_{T_2}$ at equal concentrations and temperatures. Isotopic differences between H and D in

TABLE I. (*Continued.*)

90 °C		100 °C		110 °C		120 °C	
p (mbar)	x (%)	p (mbar)	x (%)	p (mbar)	x (%)	p (mbar)	x (%)
296.8	1.8	409.3	2.0	412.7	1.8	578.0	1.9
404.9	2.2	569.3	2.3	574.1	2.1	737.7	2.1
562.0	2.8	725.2	2.8	732.6	2.4	873.7	2.2
710.1	3.7	857.0	3.1	867.4	2.5	1009.5	2.4
821.8	5.5	980.3	4.2	1000.7	2.9	1209.2	2.7
904.6	9.4	1134.5	7.7	1192.4	3.7	1483.2	3.9
967.6	19.5	1286.8	17.4	1428.0	7.6	1559.8	5.1
1000.0	35.7	1273.9	25.1	1470.5	10.5	1634.1	5.6
989.4	44.5	1295.6	29.3	1532.0	12.6	1714.5	6.4
1000.6	49.7	1312.3	34.6	1581.7	15.6	1801.4	7.5
1036.8	54.1	1335.0	40.2	1641.2	18.6	1991.8	12.7
1123.4	55.2	1409.3	53.7	1729.7	31.1		
1365.8	56.5						

TABLE II. Plateua pressures for desorption (p^D) of the PdH, PdD, and PdT system and for absorption (p^A) of the PdH and PdD system in the two-phase region $\alpha+\beta$ as a function of the temperature.

T (°C)	$p^D_{H_2}$ (mbar)	$p^A_{H_2}$ (mbar)	$p^D_{D_2}$ (mbar)	$p^A_{D_2}$ (mbar)	T (°C)	$p^D_{T_2}$ (mbar)
30		23			45	201
40		38		177	50	251
50		60	150	267	55	298
60	55	91	220	395	60	369
70	80	134	316	573	65	445
80	117	198	448	797	70	529
90	168	283	612	1079	75	630
100	237	395	840	1440	80	743
110	328	539	1144	1903	85	868
120	442	723	1513	2460	90	1000
130	594	970	2006		95	1147
140	789	1239	2600		100	1300
150	1038	1609			105	1502
160	1371	2032			110	1722
170	1768					

Pd have been observed and discussed in other papers.[23-26] Therefore, our discussion will mainly be concerned with the inequalities $x_T < x_D$ and $p_{T_2} > p_{D_2}$. The above mentioned isotopic dependence of the solubility in the α phase can be understood from a more basic standpoint by consideration of Sieverts's law for dilute solutions:

$$\ln x_T = -\Delta\bar{H}_T^\infty/(kT) + \Delta\bar{S}_T^{\infty,\mathrm{nc}}/k + \tfrac{1}{2}\ln(p_{T_2}/1\ \mathrm{bar}) , \tag{3}$$

where

$$\Delta\bar{H}_T^\infty = H_T^\infty - \tfrac{1}{2}H_{T_2}^0 \tag{4}$$

and

$$\Delta\bar{S}_T^{\infty,\mathrm{nc}} = S_T^{\infty,\mathrm{nc}} - \tfrac{1}{2}S_{T_2}^0 . \tag{5}$$

In this equation $\Delta\bar{H}_T^\infty$ and $\Delta\bar{S}_T^{\infty,\mathrm{nc}}$ are the partial molar enthalpy and entropy (without configurational contribution) of desorption at infinite dilution, H_T^∞ and $S_T^{\infty,\mathrm{nc}}$ are the partial molar enthalpy and nonconfigurational (nc) entropy of T in Pd, and $H_{T_2}^0$ and $S_{T_2}^0$ are the standard molar enthalpy and entropy of the gas phase; k is the Boltzmann constant. The different behavior of the two isotopes T and D follows from Eq. (3):

$$\ln(x_T/x_D) = -(\Delta\bar{H}_T^\infty - \Delta\bar{H}_D^\infty)/(kT) + (\Delta\bar{S}_T^{\infty,\mathrm{nc}} - \Delta\bar{S}_D^{\infty,\mathrm{nc}})/k + \tfrac{1}{2}\ln(p_{T_2}/p_{D_2}) , \tag{6}$$

with

$$\Delta\bar{H}_T^\infty - \Delta\bar{H}_D^\infty = H_T^\infty - H_D^\infty - (H_{T_2}^0 - H_{D_2}^0)/2 \tag{7}$$

and

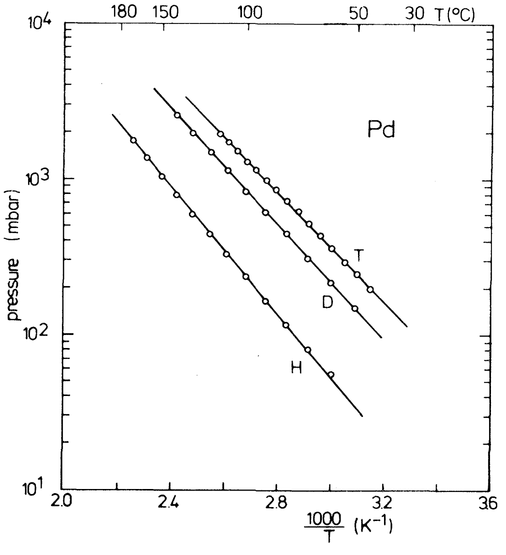

FIG. 11. Desorption plateau pressures of protium (H), deuterium (D), and tritium (T) in the two-phase region $\alpha+\beta$ as a function of reciprocal temperature.

TABLE III. $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transition enthalpies and entropies of the PdH, PdD, and PdT system for desorption and absorption processes, respectively. $X_2 = H_2$, D_2, or T_2 for PdH, PdD, and PdT, respectively.

	$\Delta H^{\beta \rightarrow \alpha}$ (kJ/mol X_2)	$\Delta S^{\beta \rightarrow \alpha}$ [(J/(K mol X_2)]	$\Delta H^{\alpha \rightarrow \beta}$ (kJ/mol X_2)	$\Delta S^{\alpha \rightarrow \beta}$ [J/(K mol X_2)]	Reference
PdH	39.0±0.5	92.5±1.3	−37.4±0.3	92.5±0.8	This work
	39.0±0.4	91.2±0.8			Ref. 18
	41.0±0.4	97.5±0.8			Ref. 2
PdD	35.4±0.5	93.4±1.3	−33.6±0.6	−93.3±1.6	This work
	37.2±0.4	97.8±0.8			Ref. 18
PdT	33.3±1.0	91.7±2.9			This work

$$\Delta \bar{S}_{\mathrm{T}}^{\infty,\mathrm{nc}} - \Delta \bar{S}_{\mathrm{D}}^{\infty,\mathrm{nc}} = S_{\mathrm{T}}^{\infty,\mathrm{nc}} - S_{\mathrm{D}}^{\infty,\mathrm{nc}} - (S_{\mathrm{T}_2}^{0} - S_{\mathrm{D}_2}^{0})/2 \tag{8}$$

The enthalpies on the right-hand side of Eq. (7) are the sum of vibrational, rotational, electronic, and nuclear contributions. Most of these contributions are small in comparison to the vibrational one. Therefore, we will consider only the vibrational energies, which are drawn in Fig. 12 for the gas molecules on the left-hand side, the atoms in the octahedral sites of the α phase in the middle, and the β phase on the right-hand side. On the left-hand side of each energy scale are plotted the zero-point energies $(n/2)\hbar\omega$; on the right-hand side the energies obtained using the Einstein formula

$$E = \frac{n\hbar\omega}{e^{\hbar\omega/kT} - 1} + \frac{n}{2}\hbar\omega , \tag{9}$$

where $\hbar\omega$ is the energy of the first harmonics of the local modes of the dissolved atoms and the gas molecules and n is the degree of freedom ($n=3$ for H,D,T in Pd and $n=1$ for the gas molecules). The vibrational zero-point energies of H_2, D_2, and T_2 are taken from Ref. 27, the energy values $\hbar\omega$ of the local modes of the H and D atoms in the α phase of PdH_x and PdD_x are from Ref. 28, and in the β phase, from Ref. 29. The zero-point energies and the values obtained with Eq. (9) for H_2, D_2, and T_2 are equal at 383.15 K due to the high-characteristic vibrational temperatures of about 6240, 4440, and 3650 K,[30] respectively (e.g, only the lowest energy level is occupied). Rotational contributions are neglected because the characteristic rotational temperature is only 85.4 K (Ref. 30) for H_2 and 42.7 K (Ref. 30) for D_2 (e.g., most of the molecular rotations are excited). Since there is not an experimentally determined local-mode frequency of T in Pd, the value was calculated using the equation $\hbar\omega_{\mathrm{T}} = \hbar\omega_{\mathrm{D}}(m_{\mathrm{D}}/m_{\mathrm{T}})^{1/2}$, where m is the reduced mass. This classical law is fulfilled for the local modes of the H and D atoms in Pd if one uses the values of Ref. 28 determined by inelastic neutron scattering. For a quantitative explanation of the isotope solubility ratio of the very dilute PdH_x and PdD_x system Oates and Flanagan[25] had to assume that the vibrational frequencies are not only mass determined, but also dependent on the force constants of the potential well for the H and D atom. In this discussion we neglect the last contribution.

With the vibration energies of Fig. 12, Eq. (7) can be written as $\Delta \bar{H}_{\mathrm{T}}^{\infty} - \Delta \bar{H}_{\mathrm{D}}^{\infty} = 11.71$ meV. Using the values listed in Ref. 7, one obtains $(-0.10k)$ (k is the Boltzmann constant) for the difference of the partial molar entropies [Eq. (8)]. Inserting this into Eq. (6) yields

TABLE IV. A and B values of the phenomenological equation $\ln(p/1\ \mathrm{bar}) = A(T) + B(T)x$ describing the relationship between pressure (p) and concentration x in the β phase of PdH_x, PdD_x, and PdT_x.

	PdH				PdD				PdT	
	This work		Ref. 18		This work		Ref. 18		This work	
T (°C)	A	B	A	B	A	B	A	B	A	B
30			32.9	46.8			29.8±0.3	44.7±0.4		
50	28.8±2.7	42.7±4.1	29.1±0.5	42.7±0.6	21.0±2.3	32.8±3.6	24.5±0.2	38.4±0.3	19.2±5.5	31.0±8.9
60	26.0±1.8	39.1±2.7			18.8±1.9	29.9±3.1			16.2±5.0	26.8±8.4
70	23.4±2.0	35.8±3.0			16.5±1.9	26.8±3.1			12.0±3.6	20.4±6.1
80	20.7±2.0	37.3±3.2			13.9±1.6	23.2±2.6				

TABLE V. Phase limits between the $\alpha+\beta$ and the β phase for PdH_x, PdD_x, and PdT_x.

T °C	PdH_x x (%)	PdD_x x (%)	PdT x (%)	PdH x (%)	PdD x (%)
50	60.2(3)	59.1(4)	58.2(5)	59.9(3) (Ref. 18)	58.7 (Ref. 18)
60	59.8(3)	58.6(4)	57.5(6)		
70	59.0(3)	57.3(4)	56.7(6)	57.5(2) (Ref. 2)	
80	58.1(3)	56.9(5)	56.0(7)		
90	57.3(4)	56.2(5)	54.8(8)		
100	56.6(4)	55.8(6)			
110	56.2(4)	55.0(6)			
120	55.5(5)	54.4(7)		54.0(3) (Ref. 2)	
130	54.7(6)				

$$\ln\left[\frac{x_T}{x_D}\right] = -\frac{135.8}{T} - 0.10 + \tfrac{1}{2}\ln\left[\frac{p_{T_2}}{p_{D_2}}\right] . \qquad (10)$$

Assuming equal pressures, it follows that x_T is smaller than x_D because the right-hand side of Eq. (10) is always negative. At equal pressures and at the temperture of 120 °C one obtains, for example, $x_T/x_D = 0.64$, which is in good agreement with our experimentally observed value of about 0.60.

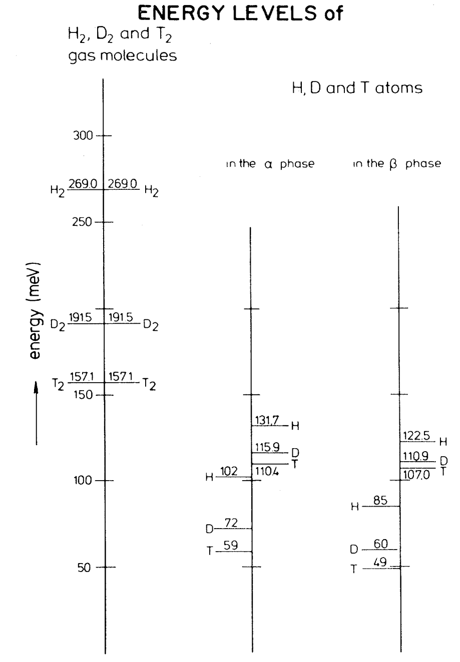

FIG. 12. Vibrational energies calculated with the formula (9) (see text) for 110 °C and zero-point energies of the H_2,D_2,T_2 gas molecules (left) (Ref. 27) and H,D,T atoms in the octahedral sites of the Pd lattice in the α phase (middle) (Ref. 28) and in the β phase (right) (Ref. 29). The zero-point energies are plotted on the left-hand side of each vertical line, the vibrational energies on the right-hand side. The atom energies are scaled up per atom for the threefold degeneracy and must be counted twice for comparison with the molecular energies.

The above equation also demonstrates that the ratio of the concentrations in the measured temperature range is mainly determined by the difference in the molar enthalpies if $p_{T_2} = p_{D_2}$. Furthermore, Eq. (10) shows that for equal concentrations $p_{T_2} > p_{D_2}$. In a similar way, the further inequalities $x_T < x_H$ and $x_D < x_H$ can also be verified.

Finally, we can qualitatively understand the isotopic dependence of the pressures in the two-phase region by considering the values listed in Fig. 12. The equation describing the behavior of the plateau pressures as a function of the temperture is

$$\ln[p_{T_2}/(1\ \text{bar})] = -\Delta H_T^{\beta\to\alpha}/(RT) + \Delta S_T^{\beta\to\alpha}/R \qquad (11)$$

with

$$\Delta H_T^{\beta\to\alpha} = H_{T_2}^0 + \frac{2}{\beta-\alpha}(\alpha H_T^{\alpha} - H_T^{\beta}) \qquad (12)$$

and

$$\Delta S_T^{\beta\to\alpha} = S_{T_2}^0 + \frac{2}{\beta-\alpha}(\alpha S_T^{\alpha} - \beta S_T^{\beta}) , \qquad (13)$$

where α and β are the concentrations at the phase limits.

$\Delta H_T^{\beta\to\alpha}$ and $\Delta S_T^{\beta-\alpha}$ represent the $\beta\to\alpha$ transition enthalpies and entropies, respectively. The ratio of the T_2 and D_2 gas pressures over palladium can be obtained from

$$\ln(p_{T_2}/p_{D_2}) = -(\Delta H_T^{\beta\to\alpha} - \Delta H_D^{\beta\to\alpha})/RT + (\Delta S_T^{\beta\to\alpha} - \Delta S_D^{\beta\to\alpha})/R \qquad (14)$$

with

$$\Delta H_T^{\beta\to\alpha} - \Delta H_D^{\beta\to\alpha} = (H_{T_2}^0 - H_{D_2}^0) + \frac{2}{\beta-\alpha}(\alpha H_T^{\alpha} - \beta H_T^{\beta} - \alpha H_D^{\alpha} + \beta H_D^{\beta}) , \qquad (15)$$

$$\Delta S_{\mathrm{T}}^{\beta\to\alpha}-\Delta S_{\mathrm{D}}^{\beta\to\alpha}=S^{0}_{\mathrm{T}_2}-S^{0}_{\mathrm{D}_2}+\frac{2}{\beta-\alpha}(\alpha S_{\mathrm{T}}^{\alpha}-\beta S_{\mathrm{T}}^{\beta}-\alpha S_{\mathrm{D}}^{\alpha}+\beta S_{\mathrm{D}}^{\beta})\ . \qquad (16)$$

In the above equations it was assumed that $\beta-\alpha$ has the same value for the different isotopes. Using $\beta-\alpha=0.53$, and again considering only vibrational contributions, one obtains $\Delta H_{\mathrm{T}}^{\beta\to\alpha}-\Delta H_{\mathrm{D}}^{\beta\to\alpha}=-26.72$ meV. For the difference $\Delta S_{\mathrm{T}}^{\beta\to\alpha}-\Delta S_{\mathrm{D}}^{\beta\to\alpha}$ we only consider $S^{0}_{\mathrm{T}_2}-S^{0}_{\mathrm{D}_2}$, because the expressions in the parentheses of Eq. (16) cancel to a first approximation. This is due to the fact that some contributions to the partial molar entropies, such as configurational or electronic, are very similar for H and D in Pd. Equation (14) can then be written as

$$\ln(p_{\mathrm{T}_2}/p_{\mathrm{D}_2})=310/T+1.0 \qquad (17)$$

with $(S^{0}_{\mathrm{T}_2}-S^{0}_{\mathrm{D}_2})/R=-1.007\,62$.[27] Equation (17) shows that $p_{\mathrm{T}_2}>p_{\mathrm{D}_2}$ since the right-hand side is always positive. Quantitatively, one obtains for the temperature of 110 °C $p_{\mathrm{T}_2}/p_{\mathrm{D}_2}=6.1$. This value is too large compared with the experimentally determined one of 1.5, but the agreement between these two values is not too bad if one considers all the simplifications made in Eqs. (15) and (16). Inserting the corresponding values of protium in Eqs. (14)–(16) yields the additional inequalities $p_{\mathrm{T}_2}<p_{\mathrm{H}_2}$ and $p_{\mathrm{D}_2}>p_{\mathrm{H}_2}$. Again qualitative agreement with the experimental results (see Fig. 11) is achieved. For a quantitative calculation of the pressure ratios in Eqs. (6) and (14), an accurate knowledge of the rotational, configurational, vibrational, and electronic contributions to the partial molar entropies and enthalpies would be necessary.

V. CONCLUSIONS

We have presented the first solubility measurements of tritium in Pd in the concentration (x) range $0.02\leq x\leq 0.65$. In the measured temperature and concentration region the phase diagram of PdT_x can be divided into three parts—the dilute α, the concentrated β, and the two-phase region $\alpha+\beta$ which is similar to the phase diagrams of PdH_x and PdD_x. Over the entire region of compositions covered by our experiments the following inequalities hold: $x_{\mathrm{T}}<x_{\mathrm{D}}<x_{\mathrm{H}}$ at equal pressures and temperatures and $p_{\mathrm{T}_2}>p_{\mathrm{D}_2}>p_{\mathrm{H}_2}$ at equal concentrations and temperatures. The $\beta\to\alpha$ transition enthalpies show a strong isotope effect. These isotopic dependences are mainly determined by the different vibrational energies of the molecules H_2,D_2,T_2 and the atoms H,D,T in Pd. For an accurate, quantitative comparison, a knowledge of all other contributions to the partial molar entropies and enthalpies of H,D,T in Pd would be necessary.

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