PHYSICAL REVIEW B VOLUME 29, NUMBER 8 15 APRIL 1984

Solubility of protium, deuterium, and tritium in the α phase of palladium

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(Received 16 December 1983)

The first solubility determinations of tritium in bulk palladium are presented for the pressure range $0.016 \leqslant p \leqslant 1.33$ bars, temperature range $60 \leqslant T \leqslant 400\,^{\circ}\mathrm{C}$, and concentration range $0.0015 \leqslant x \leqslant 0.02$ (for x in PdT_x). In addition, the first comparative study of the pressure-composition-temperature relationship of all hydrogen isotopes in Pd at low concentration is described using the same sample under identical experimental conditions. The solubility of tritium in Pd behaves as expected from the stable hydrogen isotopes. The partial molar enthalpy $\Delta\bar{H}^{\infty}_{\mathrm{T}_2}$ and the nonconfigurational entropy $\Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{T}_2}$ at infinite dilution measured during desorption decrease with increasing temperature. Furthermore, $\Delta\bar{H}^{\infty}_{X_2}$ ($X=\mathrm{H,D,T}$) shows a strong isotopic dependence, whereas $\Delta\bar{S}^{\infty,\mathrm{nc}}_{X_2}$ shows a weak one. The following inequalities are valid: $\Delta\bar{H}^{\infty}_{\mathrm{T}_2} < \Delta\bar{H}^{\infty}_{\mathrm{D}_2} < \Delta\bar{H}^{\infty}_{\mathrm{H}_2}$ and $\Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{T}_2} \leqslant \Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{D}_2} \leqslant \Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{H}_2}$. The different behavior of the solubility for H and D or H and T can be related well to the different vibrational energies of H, D, and T in the measured temperature range if one uses the vibrational energies of the H and D atoms in Pd determined by inelastic neutron scattering and extrapolates for T in Pd.

The palladium-hydrogen (PdH_x) system is the classical prototype for metal-hydrogen systems for more than one century. Together with the palladium-deuterium (PdD_x) system it is the most extensively studied metal-hydrogen alloy [see review articles (Refs. 1 and 2) and references therein]. One of the very often studied properties of PdH_x and PdD_x is the solubility behavior of H and D in Pd.[3–12] On the other hand, only little and contradictory information exists for the solubility of tritium in Pd in limited temperature (T), pressure (p), and concentration (x) ranges [Pd black, $200 \leqslant T \leqslant 400\,^{\circ}\mathrm{C}$, $7 \leqslant p \leqslant 200$ mbar, and $7.3\times10^{-4} \leqslant x \leqslant 0.0047$;[13] for bulk Pd plates of 120 μm thickness, $25 \leqslant T \leqslant 70\,^{\circ}\mathrm{C}$, $1.3 \leqslant p \leqslant 50$ mbar, and $0.0024 \leqslant x \leqslant 0.014$;[14] and for Pd foil (10 μm), $35 \leqslant T \leqslant 125\,^{\circ}\mathrm{C}$, $100 \leqslant p \leqslant 2000$ mbar, and $0.02 \leqslant x \leqslant 0.65$].[15,16] Solubility studies are of importance from a basic as well as a technological standpoint. Measurements of the properties of tritium in metals extend our knowledge of isotopic effects and can therefore test theories of metal-hydrogen systems. In addition, good knowledge of the behavior of tritium in metals is necessary for the safe storage of tritium and for the handling of large amounts of tritium in nuclear fission and fusion reactors.

In this Brief Report we report the results of the first measurements of tritium in bulk palladium in the concentration range $0.0015 \leqslant x \leqslant 0.02$, temperature range $60 \leqslant T \leqslant 400\,^{\circ}\mathrm{C}$, and pressure range $0.016 \leqslant p \leqslant 1.33$ bars. In addition, the solubility data of PdH_x and PdD_x were determined.

The experiments were performed in an all-metal UHV system especially built for safe handling of 1000 Ci tritium (10 Ci $\hat{=}$ 1 mg) and described elsewhere[16,17] and were controlled by a PDP-11 computer which controlled and measured the sample temperature and the equilibrium pressure and calculated the absorbed hydrogen concentration in the calibrated volumes. A single-sided capacitance manometer sensor (10^4-mbar range) was used for the pressure determinations.[18]

The Pd sample (purity 99.999%, purchased from Demetron, Hanau) was a wire with a diameter of 1.2 mm, etched and annealed in a UHV system.

The T_2 gas employed has a purity of 93.4 at.% T, 1.9 at.% D, and 4.7 at.% H analyzed by mass spectrometry. The experimental data obtained with this mixture of hydrogen isotopes were corrected to 100% T_2 gas by means of a program which (i) considers that the measured pressure is the sum of the partial pressures of H_2, D_2, T_2, HD, HT, and DT molecules, (ii) uses the experimentally determined relationships between p, T and x for pure H_2 and D_2, and (iii) assumes that the partial pressures of the six different molecules are in thermodynamical equilibrium and that the absorbed amount of each hydrogen isotope obeys Raoult's law. The He-3 portion of the tritium gas was negligible. The amount of He-3 generated inside the Pd sample did not influence the (p,x,T) data. The H_2 and D_2 gases obtained from FeTi-hydrogen containers[19] had isotopic purities of 99.9999 and 99.7 vol.%, respectively.

Figure 1 shows a selection of desorption isotherms of the three hydrogen isotopes (○) in Pd measured between 60 and 400 °C in steps of 20 °C at low concentrations. For tritium both the experimental data obtained with the impure tritium gas (□) and the corrected data (○) are presented. The correction shifts the experimental data to slightly higher pressure values. One sees immediately that the solubilities obey the inequalities $x_{\mathrm{T}} < x_{\mathrm{D}} < x_{\mathrm{H}}$ at equal pressures and temperatures or $p_{\mathrm{T}_2} > p_{\mathrm{D}_2} > p_{\mathrm{H}_2}$ at equal concentrations and temperatures in agreement with the observations in the $\alpha+\beta$ and β phase of the palladium hydrogen systems.[15–17] In addition, the three plots in Fig. 1 show that the solubility of H, D, and T in Pd decreases with increasing temperature at equal pressures. This means that T_2 gas molecules are absorbed in Pd exothermically like H_2 and D_2. The solubility data of T in Pd follow the normal run expected from an extrapolation of the solubility data of PdH and PdD in contradiction to the studies of Favreau, Patterson, Randall, and Salmon,[13] but in agreement with Schmidt and Sicking.[14]

The equation describing the thermodynamical equilibrium between the concentration of hydrogen in a metal and the pressure of the hydrogen gas can be written in the following way:

$$\ln\frac{p}{p_0}\left(\frac{x_s-x}{x}\right)^2 = 2\ln K_s + \frac{2}{RT}\Delta\mu \tag{1}$$

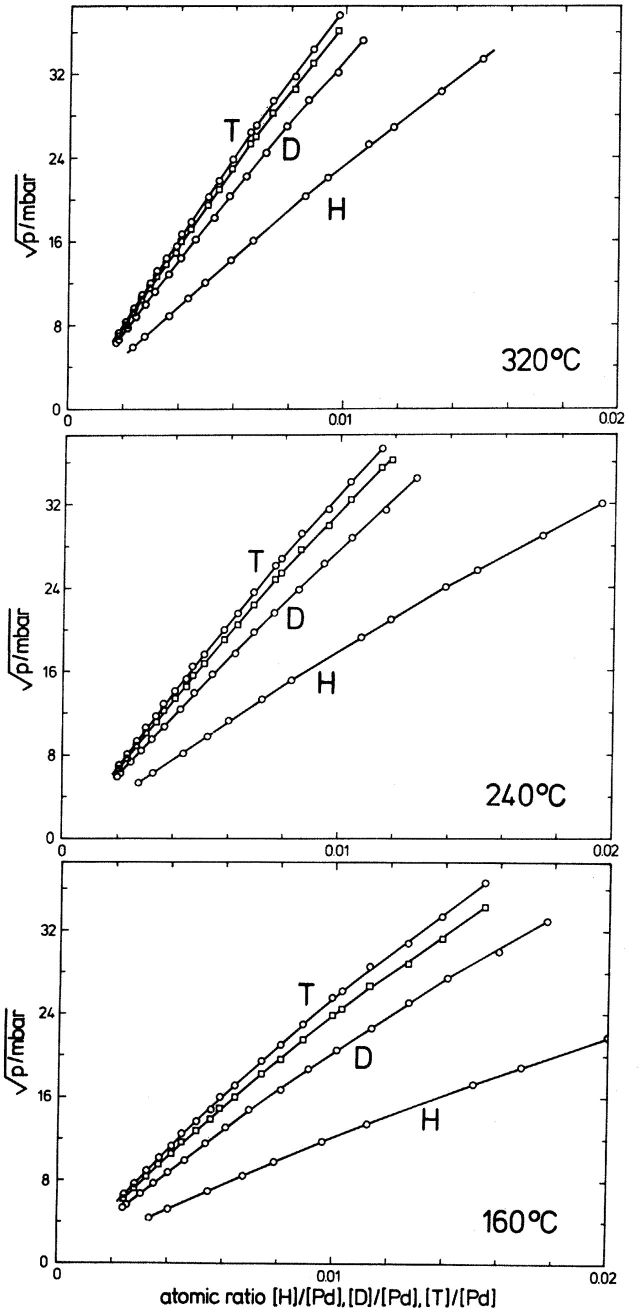

FIG. 1. Desorption isotherms for the pure hydrogen isotopes protium (H), deuterium (D), tritium (T), and the isotope mixture (93.4 at.% T, 1.9 at.% D, and 4.7 at.% H) (□) in palladium.

with

$$2\ln K_s = -\frac{\Delta\bar{H}^{\infty}_{X_2}}{RT} + \frac{\Delta\bar{S}^{\infty,\mathrm{nc}}_{X_2}}{R} . \tag{2}$$

$\Delta\bar{H}^{\infty}_{X_2}$ and $\Delta\bar{S}^{\infty,\mathrm{nc}}_{X_2}$ are the partial desorption enthalpy and entropy (without configurational contribution) of 1 mol X_2 ($X = \mathrm{H,D,T}$) at infinite dilution. $\Delta\mu$ is an excess chemical potential describing deviations from Sieverts's law, R is the gas, and K_s the Sieverts's constant. Assuming $\Delta\mu$ to be proportional to x at low concentrations and x_s to be equal to 1 for the PdX_x systems, the experimental data plotted in the way of Eq. (1) can be fitted at equal temperatures by straight lines which intersect the y axis at $2\ln K_s$. These values are plotted in Fig. 2 for the three pure hydrogen isotopes (○). The curvature of the plotted lines clearly demonstrates that the quantities $\Delta\bar{H}^{\infty}_{X_2}$ and $\Delta\bar{S}^{\infty,\mathrm{nc}}_{X_2}$ of Eq. (2) are temperature dependent. These values calculated with Eq. (2) in temperature ranges of 60 °C are listed in Table I as well as the values printed in Refs. 6, 10, 14, and 20. The agreement between the $\Delta\bar{H}^{\infty}_{X_2}$ and the $\Delta\bar{S}^{\infty,\mathrm{nc}}_{X_2}$ ($X = \mathrm{H,D}$) values of our study and the ones of the other groups is good. In addition, our $\Delta\bar{H}^{\infty}_{\mathrm{T}_2}$ and $\Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{T}_2}$ data show the same temperature dependence as the stable hydrogen isotopes. The following inequalities hold: $\Delta\bar{H}^{\infty}_{\mathrm{T}_2} < \Delta\bar{H}^{\infty}_{\mathrm{D}_2} < \Delta\bar{H}^{\infty}_{\mathrm{H}_2}$ and $\Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{T}_2} \leqslant \Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{D}_2} \leqslant \Delta\bar{S}^{\infty,\mathrm{nc}}_{\mathrm{H}_2}$. The differences between the partial molar enthalpies are large (strong isotopic effect), whereas the partial molar entropies are nearly equal (weak isotopic effect).

Ebisuzaki and co-workers[21,22] developed a model to explain the different solubilities of protium and deuterium in metals. Apart from the differences of the thermodynamic properties of the gaseous species their theory considers only vibrational contribution assuming a single frequency ν_{H} and ν_{D} for H and D atoms on the interstitial sites in the metal (Einstein approximation) and $\nu_{\mathrm{H}} = \nu_{\mathrm{D}}\sqrt{2}$ (harmonic model). Extending their theory for tritium one obtains from Eq. (1) with $\Delta\mu_{\mathrm{H}} = \Delta\mu_{\mathrm{T}}$ and $x << 1$

$$\ln\left[\frac{x_{\mathrm{H}}}{x_{\mathrm{T}}}\left(\frac{p_{\mathrm{T}_2}}{p_{\mathrm{H}_2}}\right)^{1/2}\right] = 3\ln\left(\frac{\sinh(\theta_{\mathrm{T}}/2T)}{\sinh(\theta_{\mathrm{H}}/2T)}\right) + \frac{1}{2R}(S^0_{\mathrm{T}_2} - S^0_{\mathrm{H}_2}) - \frac{1}{2RT}(H^0_{\mathrm{T}_2} - H^0_{\mathrm{H}_2}) , \tag{3}$$

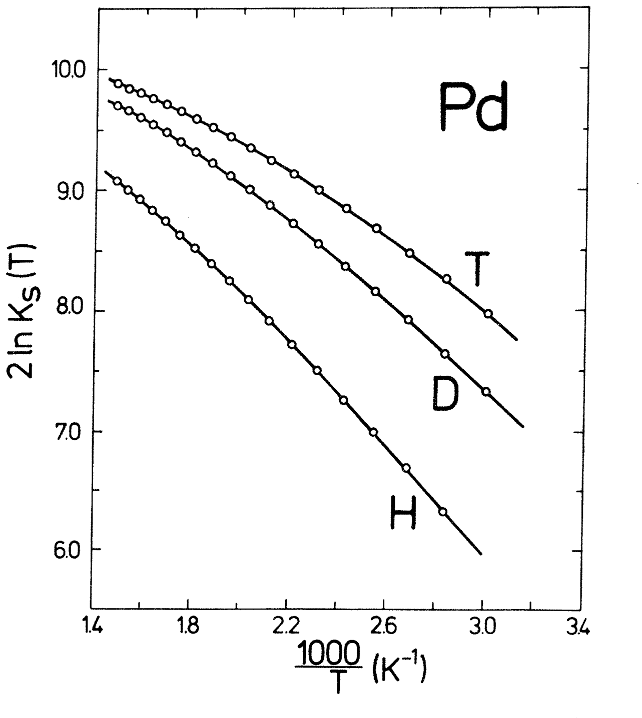

FIG. 2. Sieverts constant for protium (H), deuterium (D), and tritium (T) in palladium as a function of reciprocal temperature.

TABLE I. Partial molar enthalpies $\Delta\bar{H}^{\infty}_{X_2}$ and partial molar nonconfigurational entropies $\Delta\bar{S}^{\infty,\mathrm{nc}}_{X_2}$ at infinite dilution as a function of the temperature for the pure hydrogen isotopes (X=H,D,T).

T°C	$\Delta\bar{H}^{\infty}_{H_2}$ J/mol H_2	$\Delta\bar{H}^{\infty}_{D_2}$ J/mol D_2	$\Delta\bar{H}^{\infty}_{T_2}$ J/mol T_2	$\Delta\bar{S}^{\infty,\mathrm{nc}}_{H_2}$ J/K mol H_2	$\Delta\bar{S}^{\infty,\mathrm{nc}}_{D_2}$ J/K mol D_2	$\Delta\bar{S}^{\infty,\mathrm{nc}}_{T_2}$ J/K mol T_2	
50	19340	15780	. . .	107.1	106.2	. . .	Wicke and Nernst (Ref. 6)
50	. . .	. . .	13830	. . .	. . .	103.8	Schmidt and Sicking (Ref. 14)
50	20400	16360	. . .	110.4	109.6	. . .	Lynch and Flanagan (Ref. 20)
60.2	20550	16520	. . .	110.2	109.2	. . .	Clewley *et al.* (Ref. 10)
100	19180 ± 200	14940 ± 200	12070 ± 200	106.9 ± 0.4	105.8 ± 0.4	102.9 ± 0.4	This work
126.9	18510	15190	. . .	105.0	105.6	. . .	Clewley *et al.* (Ref. 10)
140	18340	14110	11230	104.7	103.7	100.7	This work
180	17640	13510	10390	103.1	102.3	98.8	This work
220	16690	12460	9830	101.1	100.1	97.6	This work
226.9	15985	12530	. . .	98.8	99.8	. . .	Clewley *et al.* (Ref. 10)
260	16230	11460	8820	100.2	98.2	95.6	This work
300	15010	11050	8090	98.0	97.4	94.3	This work
340	14210	9450	7021	96.6	94.7	92.5	This work
380	13190	8490	6700	95.0	93.2	92.0	This work

where θ_H (θ_T) is the Einstein temperature of protium (tritium) in Pd and $S^0_{X_2}$ and $H^0_{X_2}$ (X=H,T) are the standard molar entropies and enthalpies of H_2 or T_2 gaseous molecules.[23] The right-hand side of Eq. (3) and the analogous relation for H and D are plotted as dashed lines in Fig. 3 using the relations for harmonic oscillators: $\theta_T=\theta_H 3^{-1/2}$ and $\theta_D=\theta_H 2^{-1/2}$. The variable parameter in Fig. 3 is the Einstein temperature of θ_H of H in Pd. The solid lines show the same set of results obtained with the experimentally determined vibrational energies of H and D in the α phase of PdX [$\hbar\omega_H=68.5$ meV, $\hbar\omega_D=46.5$ meV (Ref. 24)], the extrapolated one for T ($\hbar\omega_T=37.7$ meV) and the relation $\theta_X=\theta_H\hbar\omega_X/\hbar\omega_H$ (X=D,T). The circles represent the experimentally determined values of this study. Good agreement between our experimental data and the plotted lines is obtained only for the solid lines of 800 K, which is a value very close to the Einstein temperature $\theta_H=795$ K of H in Pd. In conclusion, comparative studies of the solubilities of H, D, and T in Pd and derived thermodynamical quantities can be done in the measured temperature range considering only vibrational contributions, the Einstein approximation, and the slightly anharmonic, experimentally determined vibrational energies of H, D, and T in Pd, because the other

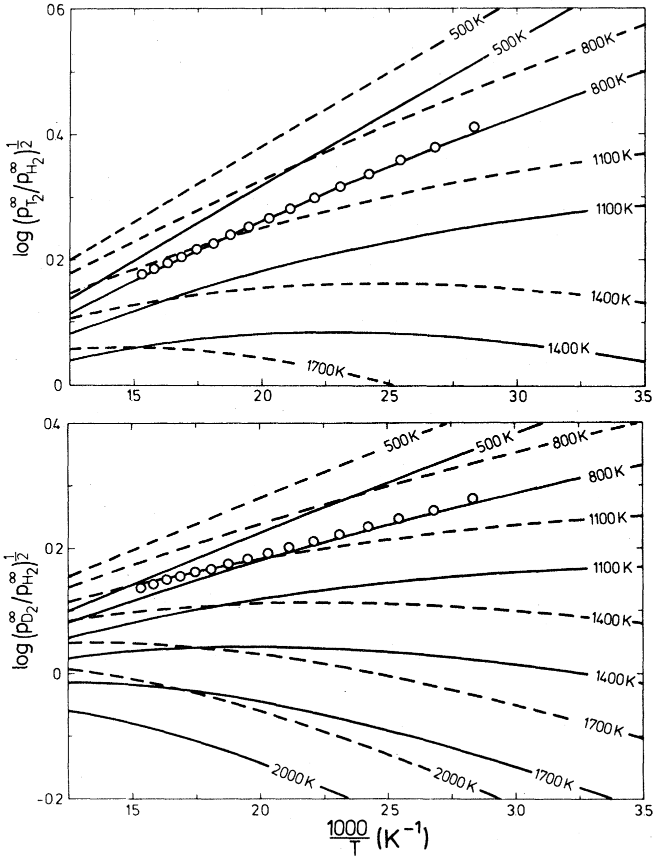

FIG. 3. Isotope solubility ratios expressed as $0.5\log(p^{\infty}_{D_2}/p^{\infty}_{H_2})$ and $0.5\log(p^{\infty}_{T_2}/p^{\infty}_{H_2})$ over reciprocal temperature. Circles represent the experimental data. The dashed (solid) lines are the result of the right-hand side of Eq. (3) using the harmonic relations (slightly unharmonic relations determined by inelastic neutron scattering and extrapolated for T in Pd) with various values of θ_H.

contributions of H, D, and T in Pd to the partial molar enthalpies or entropies cancel to a first approximation. For a quantitative comparison with the values of Table I all the other contributions in addition to the vibrational ones would have to be considered, which is not possible at present.

ACKNOWLEDGMENTS

I wish to thank D. Triefenbach for technical assistance, H. Heimbach for the analysis of the T_2 purity, and J.-M. Welter, T. Noggle, and H. Wenzl for interesting discussions.

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