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Solubility of H, D, and T in Pd at low concentrations

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The solubility measurements of H, D, and T in Pd in a large temperature range are presented. Analytic expressions are given for the equilibrium constants which describe the equilibria between hydrogen isotopes in the gas phase and hydrogen isotopes dissolved in a metal at infinite dilution. These expressions are used to predict the equilibrium constant for T in Pd from H and D data in Pd, and the predictions are compared to experimental observations. The Gibbs free energies, enthalpies, and entropies of solution of H, D, and T in Pd are calculated using these expressions. Contributions to these equilibrium constants from hydrogen isotopic species in the gas phase and the hydrogen isotopic species dissolved in Pd have been separated analytically. Parameters in these expressions, which are derived from isotope effects, define the ground-state energies of the H, D, and T species in Pd relative to the energy of atomic hydrogen at rest, i.e., the dissociation limit of H_2, D_2, and T_2. The ground-state vibrational level for H in Pd was found to be 2322.6±1.7 meV/atom below the dissociation limit for the diatomic molecule. For D in Pd the ground state was found to be 32.6±1.1 meV/atom below that of H in Pd. The ground state for T in Pd was 46.6±2.5 meV/atom below that of H in Pd. In addition, the partition functions for H, D, and T in Pd have been determined.

I. INTRODUCTION

Among the different physical properties of hydrogen in metals, the solubility of H and D in Pd (Refs. 1–12) has been investigated extensively, as discussed in review articles.[13,14] Recent experiments[15–20] have extended these measurements to the tritium isotope. The success of these investigations in comparison to studies of many other metal-hydrogen systems (e.g., V-H, Nb-H, Ta-H, etc.) is mainly due to the experimental accessibility of the Pd-H system. The noble and catalytic nature of the Pd surface, which is resistant to passivation by environmental gases, is capable of dissociating H_2 molecules, and is capable of recombining H atoms, facilitates the achievement of equilibrium. The equilibrium hydrogen pressures resulting from dilute hydrogen concentrations in Pd are easily measured over a wide temperature range (e.g., the heat of solution is not too far from zero).

We have measured the equilibrium constants for the dissolution of H, D, and T in Pd. For H and D, these measurements cover the temperature range from 20 to 1180 °C. These results are compared with existing data from the literature. For T, they cover the range of 60 to 400 °C and are the first to be measured. Using statistical models,[21–24] analytic expressions are given to describe, as a function of temperature, the equilibrium between hydrogen isotopes in the gas-phase and hydrogen isotopes dissolved in a metal at infinite dilution. The ability of these expressions to predict the behavior of T in Pd from H and D data in Pd will be demonstrated. Using these analytic expressions for the equilibrium constants, the Gibbs free energies, enthalpies, and entropies of solution of H, D, and T in Pd are calculated. These analytic expressions are the partition functions of H, D, and T in Pd. They are particularly sensitive to the ground-state energy levels for H, D, and T. This allows the relative ground-state energies for H, D, and T dissolved in Pd to be determined along with their values relative to the dissociation limit of hydrogen gas. The contribution of the vibrational energy states of hydrogen isotopes in solution in Pd to the solubility of hydrogen isotopes in Pd is discussed in the context of vibrational partition function models including those based on the recent neutron scattering measurements of the excited vibrational energy states of H and D in Pd by Rush, Rowe, and Richter.[25]

II. THEORY

A. Equilibrium between hydrogen in the gas phase and dissolved in a metal

The transfer of hydrogen between the gas phase (pressure p_{H_2}) and a metal (concentration x_H) is at thermodynamic equilibrium when the Gibbs free energy of the reactant equals that of the product. Thus,

$$G^0_{H_2} + RT\ln f_{H_2} = 2\overline{G}^{\infty}_{H} + 2RT\ln a_H \ . \tag{1}$$

$G^0_{H_2}$ is the standard Gibbs free energy of 1 mole of hydrogen gas molecules and $\overline{G}^{\infty}_{H}$ is the partial Gibbs free energy of 1 mole of hydrogen atoms in Pd at infinite dilution. The hydrogen specie is indicated by the subscript. In this paper, the Gibbs free energies are measured with respect to the energy of atomic hydrogen at rest, i.e., the dissociation limit of hydrogen molecules. This reference energy is one for which all hydrogen isotopes have the same energy. The fugacity and activity of the reactant and product species, respectively, are given by f and a. R is the gas-law constant and T is the absolute temperature in degrees kelvin. The equilibrium constant K^{∞}_{H} for the reaction is

$$\ln K^{\infty}_{\mathrm{H}}=\ln(a^{2}_{\mathrm{H}}/f_{\mathrm{H}_2})=-(2\overline{G}^{\infty}_{\mathrm{H}}-G^{0}_{\mathrm{H}_2})/RT\ . \tag{2}$$

The activity and fugacity may be expressed by the equations

$$\ln(a_{\mathrm{H}})=-\sum_{n=1}^{\infty}\alpha_{n\mathrm{H}}x^{n}_{\mathrm{H}}+\ln[x_{\mathrm{H}}/(1-x_{\mathrm{H}}/N)] \tag{3}$$

and

$$f_{\mathrm{H}_2}=p_{\mathrm{H}_2}\ , \tag{4}$$

where N is the number of sites per metal atom available to hydrogen in solution, x_{H} is the hydrogen concentration given as atomic ratio, and the $\alpha_{n\mathrm{H}}$ are the coefficients in a polynomial in x_{H}. Thus, Eq. (3) describes an activity defined such that in the limit, as x_{H} approaches zero, a_{H} approaches x_{H}. The fugacity is equated with pressure because, in these experiments, the pressure only seldom exceeded 1 atm ($=1.013$ bar). The units of pressure (p_{H_2}) are atmospheres.

In the limit of small values of x_{H}, Eq. (3) reduces to

$$\ln a_{\mathrm{H}}\cong-(\alpha_{1\mathrm{H}}-1/N)x_{\mathrm{H}}+\ln x_{\mathrm{H}}=-\alpha_{\mathrm{H}}x_{\mathrm{H}}+\ln x_{\mathrm{H}}\ , \tag{5}$$

where $\alpha_{\mathrm{H}}\equiv\alpha_{1\mathrm{H}}-1/N$, the empirically determined deviation from ideality. Combining Eqs. (2), (4), and (5) yields

$$\ln(p_{\mathrm{H}_2}/x^{2}_{\mathrm{H}})=-\ln K^{\infty}_{\mathrm{H}}(T)-2\alpha_{\mathrm{H}}(T)x_{\mathrm{H}}\ , \tag{6a}$$

or

$$\ln[p_{\mathrm{H}_2}(N-x_{\mathrm{H}})^{2}/x^{2}_{\mathrm{H}}]=-\ln[K^{\infty}_{\mathrm{H}}(T)/N^{2}]-2[\alpha_{\mathrm{H}}(T)+1/N]x_{\mathrm{H}}\ . \tag{6b}$$

The left-hand sides of Eqs. (6a) and (6b) are in the forms in which experimental data are most frequently reported in the literature. With Eq. (6a) it is possible to determine K^{∞}_{H} independently of any knowledge of N. In this paper, the values of $-\ln K^{\infty}_{X}$ are given and interpreted in terms of analytical expressions for $\overline{G}^{\infty}_{\mathrm{H}}$ and $G^{0}_{\mathrm{H}_2}$ which will be described in the following two subsections.

B. The partial molar Gibbs free energy for hydrogen dissolved in a metal

Using an extension of the theory developed by Lacher,[22] Powell[21] has shown that the following equation,

$$\overline{G}^{\infty}_{\mathrm{H}}/RT=-\ln\Xi_{\mathrm{H}}=-\ln(N\zeta\xi)-(E-E_0)/T\ , \tag{7}$$

describes the partial Gibbs free energy of one mole hydrogen atoms in a metal.

Ξ is the total partition function of hydrogen dissolved in the metal, whereas ξ is the partition function based on a well-defined vibrational model referenced to its lowest-energy state (ground state) and ζ is the partition function for all other energy states of the system referenced to the same ground-state energy as ξ.

All energy parameters in Eq. (7) have been divided by R and are in units of degrees kelvin. For a three-dimensional, isotropic, harmonic oscillator,

$$\xi=\left[\sum_{n=0}^{\infty}e^{-nC/T}\right]^{3}=(1-e^{-C/T})^{-3}\ , \tag{8a}$$

where C is the Einstein temperature of the oscillator. The factor ζ is assumed to be small and is approximated by

$$\zeta=(1+Ae^{-B/T})\ , \tag{8b}$$

representing A energy levels at energy B. This expression may represent anharmonic vibrational corrections, other vibrational manifolds, and electronic states.

The term, $E-E_0$, in Eq. (7) is the ground-state energy of hydrogen in the metal. E is the energy of the vibrational potential minimum and E_0 is the zero-point energy of the oscillator. In the case of the harmonic oscillator,

$$E_0=\tfrac{3}{2}C\ . \tag{8c}$$

In the isotope effect theory of Ebisuzaki and O'Keeffe,[26] the difference between the partial Gibbs free energies of H (protium) and D (deuterium) in Pd is given by the difference of Eq. (7) written for H and D with the assumption that the only isotope dependence for hydrogen in Pd is $C_{\mathrm{D}}=C_{\mathrm{H}}/2^{1/2}$. This is known as the "harmonic model."

Oates and Flanagan[8] used the harmonic model to analyze the H-D isotope effect for hydrogen in Pd. They proposed that H in Pd had a different spring constant than D in Pd, since the $1/2^{1/2}$ relationship predicted an isotope effect that was too large. This proposal will be referred to as the "two-spring-constant model."

Rush, Rowe, and Richter[25] have postulated a model based on their measurements of the three lowest-lying, excited vibrational energy states for H in Pd and one lowest-lying state for D in Pd. In this model, the atomic cage that forms the vibrational potential limits the amplitude of vibrations giving rise to anharmonic effects that are opposite in sense to those observed for the diatomic gas, i.e., the gap between energy levels increases with increasing quantum number. This "constrained-potential model" is described by the following sum over thermally populatable energy states:

$$\xi=\left[\sum_{n=0}^{\infty}e^{-n[\omega_0+(n+1)\beta]/T}\right]^{3}\ , \tag{9a}$$

and the zero-point energy,

$$E_0=\tfrac{3}{2}(\omega_0+\beta)\ , \tag{9b}$$

with the following values for the parameters,[25]

$$\omega_{\mathrm{H}}=580.2\ \mathrm{K},\quad \beta_{\mathrm{H}}=110.2\ \mathrm{K}\ ,$$

$$\omega_{\mathrm{D}}=\omega_{\mathrm{H}}/2^{1/2},\quad \beta_{\mathrm{D}}=\beta_{\mathrm{H}}/2\ ,$$

$$\omega_{\mathrm{T}}=\omega_{\mathrm{H}}/3^{1/2},\quad \beta_{\mathrm{T}}=\beta_{\mathrm{H}}/3\ .$$

In this paper we will analyze the measured solubilities of H, D, and T in Pd with respect to these models in an attempt to define the effects of both the known and unknown energy states on the solubility of hydrogen isotopes in Pd.

C. Standard Gibbs free energy for diatomic hydrogen gas

The best existing description of the standard Gibbs free energy of 1 mole of diatomic hydrogen gas for the temperature range above 200 K in units consistent with the measurement of gas pressure in atmospheres and the energy reference state being that of the isotopic specie at rest (0 K) is the following expression,[21]

$$G_{\mathrm{H}_2}^{0}=-\ln\Xi_{\mathrm{H}_2}=-\ln\left[\frac{LT^{7/2}}{1-e^{-J/T}}\right]-\frac{M}{T}\ . \qquad (10)$$

This equation, along with the parameters established in the literature[27–31] and listed in Table I, is one of the most accurately known and most thoroughly researched partition functions. Most of the translational-rotational partition function for a specie is given by $LT^{7/2}$. The Einstein temperature for the gas molecule is J. The parameter M is

$$M=D_0^0+B_0/3\ . \qquad (11a)$$

D_0^0 is the dissociation energy of a hydrogen molecule (e.g., the ground-state energy of the gas molecule relative to the respective atoms at rest) and has been experimentally determined for H_2, D_2, and HD (Ref. 31).

Calculations of these free-energy functions in the past[32,28] have generally used the theoretically predicted zero-point energy of the hydrogen molecule as the reference energy. The rotational constant for the hydrogen molecule is B_0. The addition of $B_0/3$ to D_0^0 in Eq. (11a) is a result of the approximation by which the rotational partition function is determined at the classical limit and does not represent a real contribution to the ground-state energy. Equations (10) and (11a) merely give a simple analytical form for the partition function that is valid for temperatures above 200 K. Mayer and Mayer[33] indicate that the validity of this expression can be extended to temperatures as low as 90 K by the use of

$$M=D_0^0+B_0/3+B_0^2/(62.6\ \mathrm{T})\ . \qquad (11b)$$

However, problems (arising from the achievement of equilibrium for the nuclear spin states of the gas-phase molecules) would have to be dealt with theoretically and experimentally prior to the actual application of this model to temperatures in the vicinity of 100 K.

The values L, J, M, D_0^0, and B_0 calculated from or taken from the data given in Refs. 27–30 are listed in Table I for the various isotopic species of hydrogen molecules.

Equilibrium constants for the formation of the gaseous species HD, HT, and DT calculated using these parameters are in good agreement with those reported by Jones.[32]

D. Analytical expression for the equilibrium constant, partial molar enthalpy, and partial molar entropy of hydrogen dissolved in the metal

Combining Eqs. (2), (7), (8a), (8b), and (10) yields the following analytical equation for the equilibrium constant:

$$\ln K^{\infty}=2\ln\left[\frac{N(1+Ae^{-B/T})}{(1-e^{-C/T})^3}\right]+2\frac{E-\frac{3}{2}C}{T}-\ln\left[\frac{LT^{7/2}}{1-e^{-J/T}}\right]-\frac{M}{T}\ . \qquad (12)$$

The partial Gibbs free energy $\Delta\bar{G}^{\infty}$, the partial enthalpy $\Delta\bar{H}^{\infty}$, and the partial entropy $\Delta\bar{S}^{\infty}$ of solution of hydrogen in the metal per 1 mole hydrogen gas at infinite dilution can be readily calculated using the Gibbs-Helmholtz relationship as shown below:

$$\Delta\bar{G}_{\mathrm{H}}^{\infty}=(2\bar{G}_{\mathrm{H}}^{\infty}-G_{\mathrm{H}_2}^{0})=-RT\ln K_{\mathrm{H}}^{\infty}\ , \qquad (13)$$

$$\Delta\bar{H}_{\mathrm{H}}^{\infty}=-R\left[\frac{\partial(\ln K_{\mathrm{H}}^{\infty})}{\partial(1/T)}\right]_{p,x}\ , \qquad (14a)$$

$$\Delta\bar{H}_{\mathrm{H}}^{\infty}=R\left[-2E+3C+\frac{6C}{e^{C/T}-1}+\frac{2AB}{e^{B/T}+A}+M-\frac{7T}{2}-\frac{J}{e^{J/T}-1}\right]\ , \qquad (14b)$$

and

$$\Delta\bar{S}_{\mathrm{H}}^{\infty}=\Delta\bar{H}_{\mathrm{H}}^{\infty}/T+R\ln K_{\mathrm{H}}^{\infty}\ . \qquad (15)$$

Equation (12) may be fit to the equilibrium constants determined from experimentally observed Sievert's constants [Eqs. (6a) and (6b)]. The analytical form of the model allows the differentiation step associated with the Gibbs-Helmholtz relationship to be executed in a straightforward manner, yielding the enthalpies and entropies of solution as a continuous function of temperature. The free-energy-function for hydrogen in the metal can be

TABLE I. List of the parameters used to calculate the free-energy functions for the isotopic species of diatomic hydrogen gas at 1 atm pressure using Eqs. (10) and (11).

Molecular species	L ($\mathrm{K}^{-7/2}$)	J (K)	M[a] (K)	D_0^0 (K)	B_0 (K)
HH	4.293×10^{-4}	5986	51 994.9	51 966.5	85.348
HD	2.093×10^{-3}	5225	52 402.2	52 380.8	64.269
HT	3.614×10^{-3}	4940	52 552.1	52 532.9	57.187
DD	2.406×10^{-3}	4307	52 888.2	52 873.9	43.027
DT	8.041×10^{-3}	3948	53 076.1	53 064.1	35.927
TT	6.582×10^{-3}	3548	53 285.6	53 276.0	28.819

[a] $M=D_0^0+B_0/3$ per Eq. (11a).

analytically separated from that of hydrogen gas, allowing the partition function for hydrogen in the metal to be measured experimentally. This partition function forms a framework within which contributions, of the various energy states of hydrogen in the metal to the macroscopic properties of the metal-hydrogen system, can be interpreted.

III. EXPERIMENTAL PROCEDURES

The solubility measurements of H and D in Pd were performed with two different experimental apparatuses, one built at the Oak Ridge Y-12 Plant by Powell[21,24] and the other at the Kernforschungsanlage Jülich by Lässer *et al.*[17,18] The system at Jülich was also used to determine the solubility of T in Pd. Both experiments yielded data points of the form (x_X, p_{X_2}, T) from which α_X and K_X^∞ are determined using Eq. (6).

A. Experiment done at the Kernforschungsanlage Jülich

The experiments determined the quantity of hydrogen absorbed by a known amount of metal by ideal gas-law calculations of the difference between the gas expanded from a known volume and the gas remaining in the volume containing the metal at some controlled temperature. This apparent volume containing the sample at temperature was calibrated against the known volume as a function of sample temperature using an inert gas such as He or Ar.

Experiments were carried out by making a single addition of hydrogen to the Pd and incrementally changing the temperature. This method minimizes the amount of hydrogen transferred between the Pd sample and the gas phase during the reestablishment of equilibrium and accelerates the achievement of equilibrium. Care was taken to determine that equilibrium was established before incrementing temperature.

Figure 1 shows a schematic drawing of the experimental setup used to determine the solubility of H, D, and T in Pd. The main components are (1) 1000-Ci UT_X storage container, (2) sample chamber, (3) capacitance manometer sensor (10 000-Torr full scale and 0.05% absolute accuracy), (4a) iron-titanium storage containers for hydrogen and (4b) for deuterium, (5) ion getter pump, (6) turbo pump, (7) rotary pump, and (8) extension volume. The whole apparatus is built of stainless steel and components of the equipment which have to be heated are surrounded by double-walled cylinders which are cooled by water in a closed loop. Therefore, permeation of tritium is drastically reduced by the cold walls and, eventually, permeated tritium is captured in the circulating water which is renewed every half-year. The use of a single-sided capacitance manometer sensor is essential for correct p_{T_2} readings.[34] The thick lines in Fig. 1 represent the volume used for the determination of the pressure, concentration, and temperature relationship.

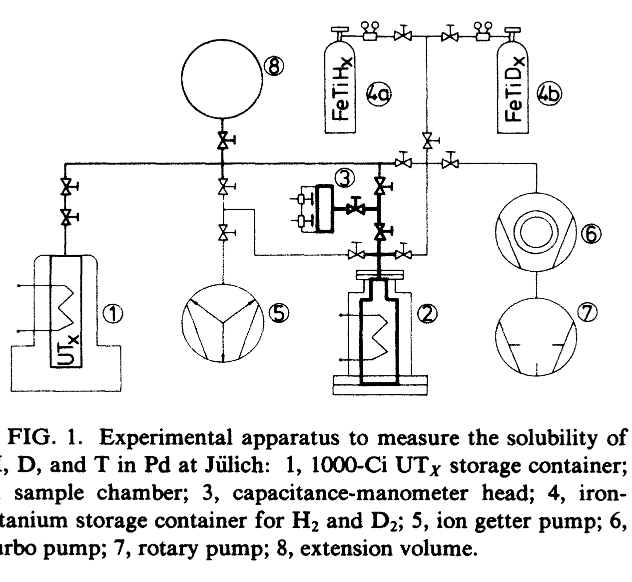

FIG. 1. Experimental apparatus to measure the solubility of H, D, and T in Pd at Jülich: 1, 1000-Ci UT_X storage container; 2, sample chamber; 3, capacitance-manometer head; 4, iron-titanium storage container for H_2 and D_2; 5, ion getter pump; 6, turbo pump; 7, rotary pump; 8, extension volume.

The purity of the Pd samples was better than 99.99% with the main impurities being Fe, Ca, and Ag. The form was a wire with a diameter of 1.2 mm. The purity of the T_2 gas used was 93.4 at.% T, 1.9 at.% D, and 4.7 at.% H, as determined by mass-spectrometric analysis. The data shown here are corrected for the slightly contaminated tritium gas mixture by an extrapolation to 100% pure T_2 gas. The amount of ^{3}He in the T_2 gas was smaller than 0.1 at.%. This was achieved by repeated heating and cooling cycles of the 1000-Ci UT_X storage container and removal of the ^{3}He not absorbed in the cold UT_X bed. The influence of ^{3}He generated inside the Pd sample on the solubility of T in Pd was also negligible. The H_2 and D_2 gases had isotopic purities of 99.999 and 99.7 vol%, respectively.

B. Experiment done at the Oak Ridge Y-12 Plant

The apparatus used by Powell[21,24] was very similar to that used at Jülich with the main differences being the use of two capacitance manometers and the absence of the tritium capability and precautions. A 1000-Torr full-scale, 0.05%-absolute-accuracy manometer was mounted to the gas-supply volume, and a 10-Torr full-scale, 0.05%-absolute-accuracy manometer was mounted as part of the sample volume. Another difference was the use of an externally heated aluminum silicate tube to contain the sample, allowing an upper temperature limit of 1500 K. The Pd sample (99.96% pure) consisted of 28.265 g of 0.25-mm-thick foil. The major impurity was Pt (0.02%) with no other elemental impurities being present at levels above 0.002% as determined by spark-source mass spectroscopy. H_2 (99.999% pure) and D_2 (99.8% D, 99.999% hydrogen isotopes) filtered through 200 mm of UH_3 or UD_3 powder was expanded onto the sample from a 45.7 mL volume. Ar (99.99% pure) was used to measure the apparent sample volume as a function of sample temperature. With the exception of the 10-Torr manometer, this apparatus, the calibration procedures, and the measurement procedures have been described in detail.[21,24] Data were acquired using the single-expansion, temperature-increment method at x_X values near 0.0013 atom ratio (first experiment) and near 0.0007 atom ratio (second experiment) for each isotope. Direct absorption isotherm measurements for the concentration range of

$0.0001 < x_X < 0.02$ were made from which K_X^{∞} and α_X were determined. Data obtained by the temperature increment method were corrected for concentration effects using α values obtained from the isothermal measurements.

IV. RESULTS, ANALYSIS, AND DISCUSSION

The experimental results obtained by Powell at Oak Ridge and Lässer at Jülich are shown as activity parameters in Fig. 2 and as equilibrium constants in Fig. 3, with both plotted as functions of reciprocal absolute temperature.

A. Activity parameters for hydrogen in palladium

The activity-parameter data of both experiments shown in Fig. 2 are in good agreement. They also agreed, within experimental error, with those values predicted by the equation for α proposed by Wicke and Nernst[4] that are written in terms of the activity parameter α in

$$\alpha_X=(2265/T)(1+T_X/T)-1 \ , \qquad (16)$$

where $X=\mathrm{H}$ or D, $T_{\mathrm{H}}=445$ K, and $T_{\mathrm{D}}=400$ K.

B. Equilibrium constants for hydrogen in palladium

Figure 3 gives the equilibrium constant data as a function of reciprocal absolute temperature, demonstrates the excellent agreement between the two laboratories for $-\ln K_{\mathrm{H}}^{\infty}$ and $-\ln K_{\mathrm{D}}^{\infty}$ measurements, and shows the agreement for $-\ln K_{\mathrm{T}}^{\infty}$ with a parametrized version of Eq. (12). Figure 3 also demonstrates the ability of Eq. (12) to describe the observations using the parameters listed in Table II (see solid lines).

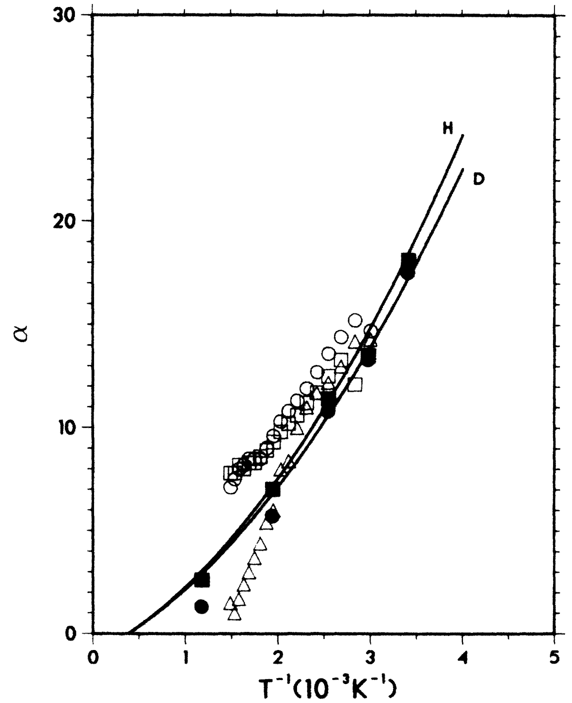

FIG. 2. The temperature dependence of the activity parameters (α_X) for hydrogen isotopes in Pd. ■, data for hydrogen by Powell; ●, data for deuterium by Powell; ○, data for hydrogen by Lässer; □, data for deuterium by Lässer; △, data for tritium by Lässer; —— (upper curve), equation for hydrogen by Wicke and Nernst, Ref. 4; —— (lower curve), equation for deuterium by Wicke and Nernst, Ref. 4.

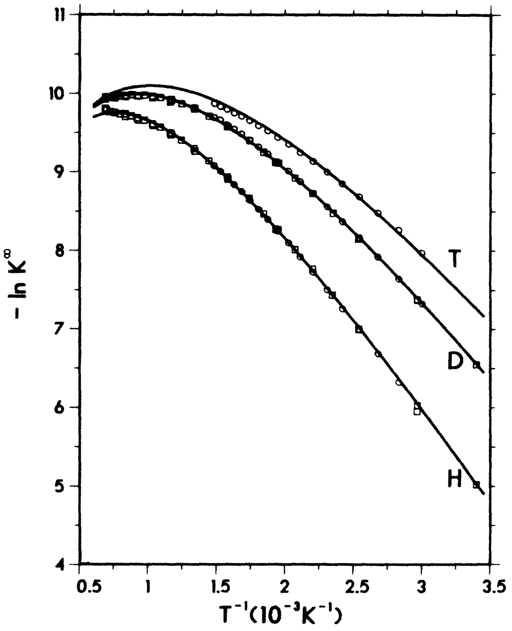

FIG. 3. The temperature dependence of the equilibrium constants (K_X^{∞}) for the indicated hydrogen isotopes in Pd. □, data by Powell; ○, data by Lässer; ——, Eq. (12) using parameter sets 1, 2, and 4, Table II.

1. Fitting procedure for determination of the parameters in Eq. (12)

The parameters used to describe the $-\ln K^{\infty}$ data in terms of Eq. (12) were selected using a proprietary nonlinear least-squares program[35] executed on an IBM 3033 computer located at the Oak Ridge National Laboratory.

Equation (12) has some very interesting properties with respect to selecting the five parameters (N,A,B,C,E) using a regression analysis. At high temperatures, all parameters may contribute significantly to the value of $-\ln K_X^{\infty}$ with N constrained to be a small integer. This is a relatively hopeless situation for uniquely determining the parameters given a single data set as a basis for fitting the curve to the parameters. At low temperatures, however, the first term in Eq. (12) becomes independent of temperature and the fit must be achieved by varying N (constrained to be a small integer) and $E-3/2C$ (a rotation about $1/T=0$), i.e., very stringent conditions for limiting the possible values for $E-3/2C$. Simple isotope-dependent relationships between the various parameters for the data for all three isotopes may also be used, but Clewley *et al.*[7] have demonstrated that the harmonic assumption used by Ebisuzaki and O'Keeffe[26] is not sufficient. The problem was approached using the assumption that hydrogen dissolved in α-Pd-H is similar to hydrogen in β-Pd-H[36] and, thus, $N=1$ for octahedral site occupan-

TABLE II. List of the parameters A, B, C, E, and N used to calculate Sievert's constant with Eq. (12) for PdX (X=H,D,T).

No.	X	N	A	B (K)	C (K)	E (K)	$E-1.5C$ (K)	σ[b]
1	H	1	1.981	768.0	800.0	28 145.0	26 945.0	0.023
2	D	1	1.933	664.0	565.7	28 175.4	27 326.9	0.015
3	T	1	2.280	677.0	461.9	28 182.3	27 489.5	0.010
4	T[a]	1	1.912	617.9	461.9	28 188.9	27 496.0	0.029

[a] Parameters for T were determined by scaling the parameters for H and D inversely as the square root of the isotopic mass.

[b] The standard deviation (σ) is the square root of the variance of the data relative to Eq. (12).

cy. Values of C were chosen that were near those determined by neutron spectroscopy. The nonlinear least-squares routine then determined the best values for A, B, and E for a given data set. Table II gives the results of such a fit based on $C_H=800$ K, $C_D=(800\text{ K})/2^{1/2}$, and $C_D=(800\text{ K})/3^{1/2}$.

Many other variations in the fitting routine were tried, including fixing the value of C_H at values ranging from 700 to 900 K, fixing the value of A at 2.000, substituting the model proposed by Rush, Rowe, and Richter [Eq. (9)][25] for the harmonic model [Eq. (8)], and fitting the data sets measured by each author separately. All these fits yielded descriptions of the data set used with a precision comparable to that in Table II and with a considerable variation in the selected parameters A, B, and E for each model and data set. Since high-temperature data are the main factor in determining the parameters A and B, the fits of Lässer's data (333–673 K) led to extremely precise fits to the data that, when extrapolated to high temperatures, often deviated markedly from the behavior of the high-temperature data for H and D. Parameter sets 1, 2, and 4 in Table II were chosen to describe the data because the tritium parameters could be predicted from the H and D parameters by a simple extrapolation inversely proportional to the square root of the isotopic mass and because the calculated values of tritium extrapolated to high temperature in a reasonable manner. The only temperature region where the calculated curves and the data deviate by an amount greater than experimental error is above 1000 K, where the term containing parameters A and B [Eq. (8b)] no longer satisfies the condition that it is small.

2. *Comparison of these equilibrium constant measurements with those determined by others*

Generally good agreement is observed for data in the literature.[1,4,7,12,15] The largest differences are with respect to the low-temperature extremes of the data (500–600 K) for H of Sieverts and Zapf[1] and of Labes and McLellan[12] and the data for T (273–343 K) by Schmidt and Sicking,[15] where their measurements of $\ln K_X^\infty$ are greater than those presented here by approximately 0.45. The present data are in excellent agreement with the isotope effect reported by Clewley *et al.*,[7] but their solubilities are slightly greater. Their data can be described using the parameters in Table II if the parameter E for H and for D is increased by 17 K. The H data by Wicke and Nernst[4] are in excellent agreement with that of the authors, whereas their values for D are in agreement with the results of Clewley *et al.*[7]

3. *Ground-state energies and partition functions of H, D, and T in Pd*

The variation of E independently of C in our curve-fitting routine is equivalent to adjusting the ground-state energy level of the hydrogen specie in the metal ($E-3/2C$, determined with respect to the vacuum level) independently for each isotope. In Fig. 4 the values for this ground-state energy, determined from the various as-

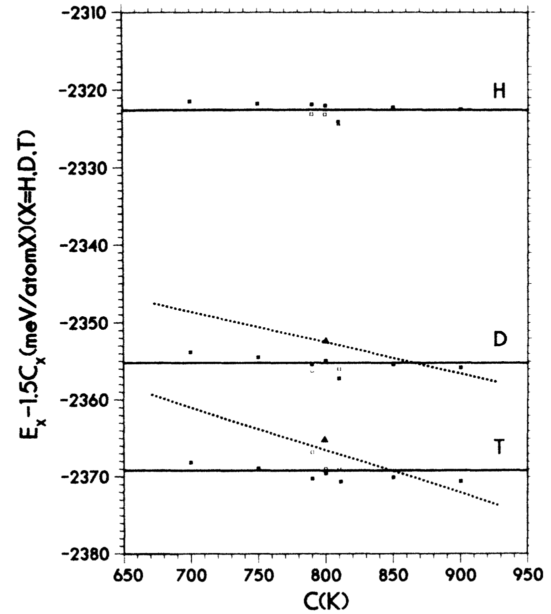

FIG. 4. The ground-state energy levels for H, D, and T in Pd as determined from fitting the equilibrium constant data to the harmonic model as a function of assumed values for the Einstein temperature C. [In order to make the points more distinguishable, data at 810 K were obtained using the model by Rush, Rowe, and Richter (Ref. 25) and data at 790 K were obtained using the harmonic model with the parameter A fixed at $A=2.000$ and $C=800$ K.] ■, data by Powell; □, data by Lässer; — — —, predicted by the harmonic model for D and T relative to H; ▲, predicted by the model of Rush, Rowe, and Richter (Ref. 25) for D and T relative to H; ——, average value of data by Lässer and Powell.

sumptions for the vibrational model, are plotted as a function of the Einstein temperature used in the particular curve fit. The results expected for the Rush-Rowe-Richter[25] model and the harmonic model is also shown in Fig. 4. The curve fitting yielded the same values for the ground-state energy of the hydrogen specie independently of the choice of model or the description of the sum over the thermally populated energy states.

Averaging all the values for $E-3/2C$ for hydrogen from Fig. 4 indicates that the ground state for hydrogen dissolved in Pd at infinite dilution lies $26\,952.2\pm18.9$ K (2322.6 ± 1.7 meV) below the dissociation limit for one-half mole of H_2 gas. The ground state for D in Pd lies 378.8 ± 12.3 K (32.6 ± 1.1 meV) below that of H in Pd. The ground state for T in Pd lies 541.0 ± 29.0 K (46.6 ± 2.5 meV) below that of H in Pd.

Thus, we have successfully separated the first and second terms in Eq. (12), yielding a measurement of the ground-state vibrational energy of hydrogen isotopes in Pd as well as the temperature dependence of the sum of the populations of the thermally populated energy states of the system. These terms are shown in Figs. 5, 6, and 7, respectively, for H, D, and T, using

$$\ln(\zeta\xi)=\ln[(1+Ae^{-B/T})(1-e^{-C/T})^{-3}]\;, \tag{17}$$

and the parameter sets 1, 2, and 4 from Table II. These figures also show the contributions of the last term in parentheses in Eq. (17) and the contribution from those vibrational energy states that have been experimentally determined by neutron spectroscopy[25,37] using Eq. (9a) for $n\leq2$ for H and $n=1$ for D.

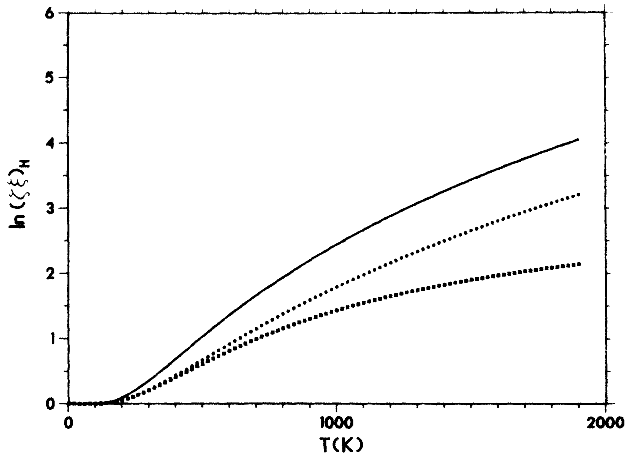

FIG. 5. The contributions of the sum over the thermally populatable energy states for hydrogen (H) in Pd to the equilibrium constant. Upper curve, total contribution based on Eq. (17) and parameter set 1, Table II; middle curve, contribution of the C term only [see Eq. (8a)]; lower curve, contribution of the states attributable to the energy levels determined by neutron spectroscopy by Rush *et al.* (Ref. 25) [Eq. (17) with Eq. (9a) for $n\leq2$].

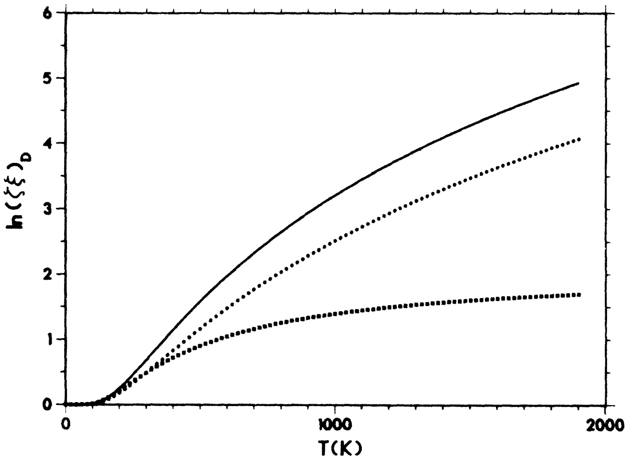

FIG. 6. The contributions of the sum over the thermally populatable energy states for deuterium (D) in Pd to the equilibrium constant. Upper curve, total contribution based on Eq. (17) and parameter set 2, Table II; middle curve, contribution of the C term only [see Eq. (8a)]; lower curve, contribution of the states attributable to the energy levels determined by neutron spectroscopy by Rush *et al.* (Ref. 25) [Eq. (17) with Eq. (9a) for $n=1$].

4. *The partial Gibbs free energies, enthalpies, and entropies for H, D, and T in Pd*

Having defined Eq. (12) by parameters, $\Delta\bar{H}_X^\infty$ and $\Delta\bar{S}_X^\infty$ are calculated as continuous functions of temperature and displayed for all three isotopic species in Figs. 8 and 9. For these calculations, the low-temperature correction given in Eq. (11b) was used. Note that both $\Delta\bar{H}_X^\infty$ and $\Delta\bar{S}_X^\infty$ have minima corresponding to the region of temperature where the role of the thermal population of vibrational states of hydrogen in palladium becomes important. In Fig. 8, the values of $\Delta\bar{H}_X^\infty$ determined calorimetrically by Boureau *et al.*[9–11] are shown to be in agreement with those calculated on the basis of this present work. Figure 9 gives the values of $\Delta\bar{S}_X^\infty$ determined directly from measured values of $\Delta\bar{G}_X^\infty$ and $\Delta\bar{H}_X^\infty$ by Boureau *et al.*[9–11] Values of these thermodynamic functions reported in the literature by other workers,[1,4,7,12,15] determined by differentiating $\ln K_X^\infty$ data, are not shown

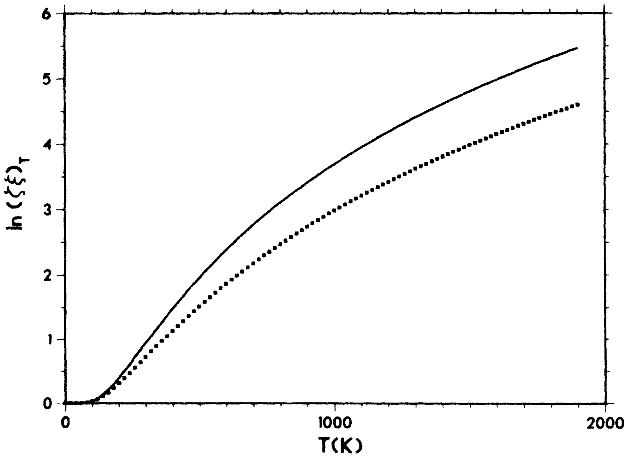

FIG. 7. The contributions of the sum over the thermally populatable energy states for tritium (T) in Pd to the equilibrium constant. Upper curve,total contribution based on Eq. (17) and parameter set 4, Table II; lower curve, contribution of the C term only [see Eq. (8a)].

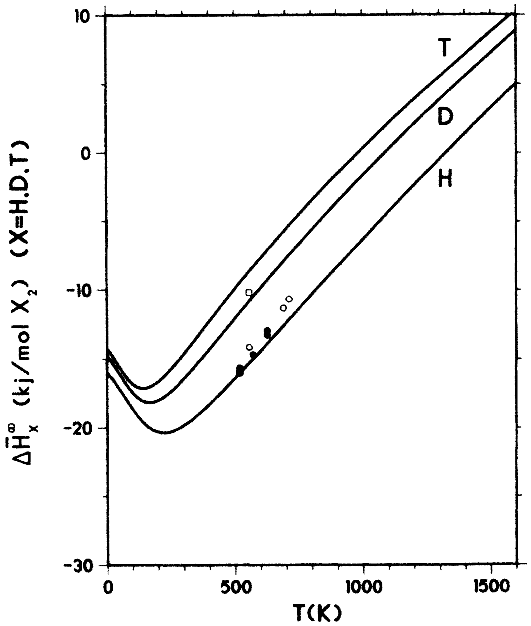

FIG. 8. The partial enthalpy per mole X_2 (pressure in atmospheres) for the dissolution of X (X=H,D,T) in Pd. ○, calorimetric data (H) from Boureau *et al.*, Ref. 10; □, calorimetric data (D) from Boureau *et al.*, Ref. 9, with approximate correction based on Ref. 10; ●, calorimetric data (H) from Picard *et al.*, Ref. 11.

in Figs. 8 and 9.

The calorimetric measurements by Boureau *et al.* evolved as a series of three papers indicated as Refs. 9–11. Their first work contained one value for $\Delta\bar{H}^{\infty}_{\mathrm{D}}$. Their second paper demonstrated a very significant improvement in their experimental accuracy over the first results, but these improvements were not applied to their results for D. The one data point in Fig. 8 for $\Delta\bar{H}^{\infty}_{\mathrm{D}}$ was assigned using the assumption that the improvements made in their measurements would not have changed the value of $\Delta\bar{H}^{\infty}_{\mathrm{H}}-\Delta\bar{H}^{\infty}_{\mathrm{D}}$. The agreement between the results of this assumption and the calculated values for $\Delta\bar{H}^{\infty}_{\mathrm{D}}$ supports this assumption.

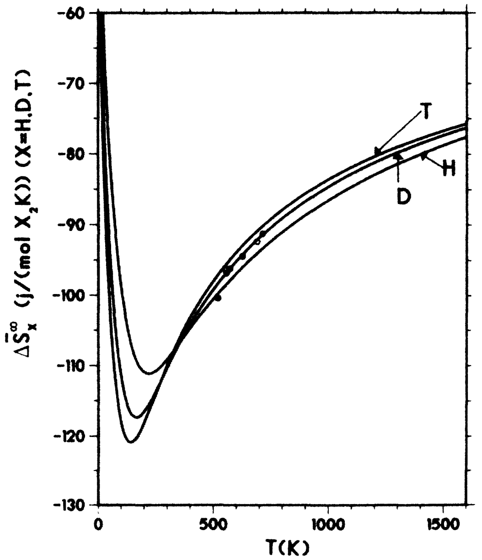

FIG. 9. The partial entropy per mole X_2 (pressure in atmospheres) for the dissolution of X (X=H,D,T) in Pd. ○, calorimetric data (H) from Boureau *et al.*, Ref. 10; □, calorimetric data (D) from Boureau *et al.*, Ref. 9, with approximate correction based on Ref. 10; ●, calorimetric data (H) from Picard *et al.*, Ref. 11.

C. Vibrational energy level diagram for hydrogen isotopes in Pd and in the gas phase

Figure 10 gives an energy-level diagram for hydrogen isotopes in palladium based on the ground-state energies determined in this work, the experimentally determined levels reported by Rush, Rowe, and Richter,[25] and the levels predicted by the constrained-potential model. These predicted levels were included to show how a slight perturbation tends to split degeneracies and, when coupled with the decreased energy spacings resulting from the heavier isotopes, leads to many closely spaced energy levels for tritium. The one-dimensional potential wells were calculated on the basis of the simple harmonic model to demonstrate the approximate amplitude of the vibrations.

These energy-level diagrams were also given to demonstrate the number of states that contribute measurably to the sum over the thermally populated energy states that constitutes the partition function for hydrogen in palladium. At elevated temperatures, the thermally populated states enhance the value of K^{∞}_{X} by a factor greater than 100. The "unknown" energy states contribute to this by more than a factor of 5 for H. There is probably a significant contribution to these unknown energy states from the electronic interaction between the solute specie and the electronic population near the Fermi level of Pd that obviously undergoes significant changes at elevated temperatures.

Figure 10 displays estimates of the vibrational potential minima that result from the range of E values determined by fitting the data to the various models. The wide range

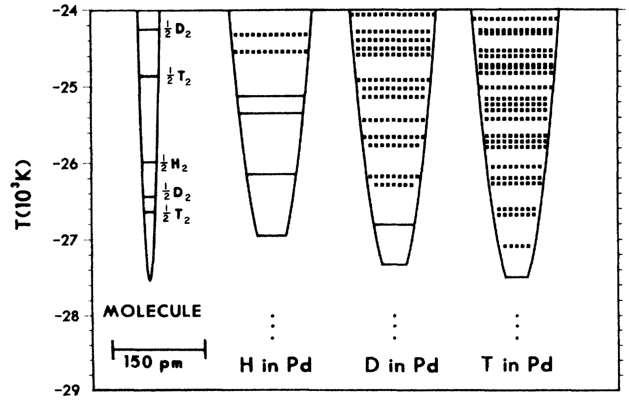

FIG. 10. Energy-level diagram of the hydrogen species considered in this work. ——, known energy states of the hydrogen-in-palladium system from this work and that of Rush *et al.*, Ref. 25, and Huber and Herzberg, Ref. 29; — — —, energy states proposed by Rush *et al.*, Ref. 25; ⁝, approximate locations of vibrational potential minima.

of these estimates reflects the lack of knowledge as to why the ground states of D and T in Pd are significantly lower, relative to H, than those predicted by the postulated vibrational potential models.

V. CONCLUSIONS

The pressure-temperature-concentration relationships for hydrogen isotopes, including H, D, and T, dissolved in the α phase of the PdX (X=H, D, T) system, have been determined experimentally for concentrations below 0.02 atom ratio and described in terms that can be readily adapted to precise numerical calculations. Equilibrium constants, thermodynamic functions, and mixed-isotope relationships can be calculated. The partition functions for hydrogen isotopes dissolved in Pd have been determined separately from that for the gas-phase species. These partition functions have been resolved into the ground-state energy and the sum over the thermally populated energy states for H, D, and T. The ground-state vibrational level of H in Pd was found to be 2322.6 ± 1.7 meV/atom H below that of the dissociation limit of hydrogen gas molecules. The ground states of D and T in Pd lie, respectively, 32.6 ± 1.1 and 46.6 ± 2.5 meV/atom below that of H in Pd. Energy levels above the ground state could not be uniquely resolved on the basis of this thermodynamic data, but the sum over the thermally populated excited energy states was greater than that predicted by simple vibrational models.

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