

## Thermodynamic Aspects of Hydrogen Motions in Dilute Metallic Solutions

G. BOUREAU\* AND O. J. KLEPPA†

*The James Franck Institute and Department of Chemistry, The University of Chicago, Chicago, Illinois 60637*

AND P. D. ANTONIOU

*The James Franck Institute and Department of Physics, The University of Chicago, Chicago, Illinois 60637*

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Mainly using available precise thermodynamic data for dilute solutions of hydrogen and deuterium in palladium and in the Pd<sub>0.9</sub>Ag<sub>0.1</sub> alloy, we show that the description of the hydrogen atoms as simple harmonic oscillators represents a very crude first approximation only. Similarly, the other simple models which have been advanced are not consistent with all the available thermodynamic data. We propose to consider hydrogen dissolved in metals at high temperature as a very dense liquid rather than as a gas (as is usually done). We have also been led to conclude that the force constant for hydrogen in fcc metals should be slightly larger than for deuterium.

### 1. Introduction

The increasing amount of precise data, often based on new experimental techniques, has allowed a better understanding of metal-hydrogen systems (1-4). Until quite recently, the thermodynamic treatment of such systems generally has been based on the simple Lacher model proposed some 40 years ago (5). In recent years, however, it has become increasingly apparent that this model is much too crude. Even in the simple case of very dilute solutions, two difficulties have been recognized:

1. It is not possible in a convincing way to explain the magnitude of the excess entropy,  $\bar{S}_H - R \ln[(1-x)/x]$  (6, 7), and

2. The simple Einstein model is not consistent with the thermodynamic measurements of the isotope effect (8-10).

The purpose of the present paper is to study the origin of these two discrepancies. In connection with this, we also want to consider the information that thermodynamic measurements can provide with respect to the motion of the dissolved hydrogen atoms in very dilute solutions. In the next two sections we discuss these problems in greater detail for the most extensively studied system, palladium-hydrogen. In Sections IV, V, and VI we discuss three types of models which have been advanced previously, i.e., the transition toward a fluid state, the adoption of different force constants for hydrogen and deuterium, and the use of anharmonic potentials. In Section VII we finally propose a qualitative

\* Permanent address: University of Paris-Sud, Bâtiment 415, 91405 Orsay Cedex, France.

† To whom all correspondence should be addressed.

representation which exhibits the correct behavior and allows us to make a distinction between solutions in fcc and bcc metals.

## II. The Excess Entropy

Following O'Keefe and Steward (11) we shall assume that it is possible to disregard the coupling between the various "degrees of freedom" for hydrogen in a metal. We accordingly write for the partial molar excess entropy of hydrogen,  $\bar{S}_H^E = \bar{S}_H - R \ln[(1-x)/x]$ :

$$\bar{S}_H^E = \bar{S}_1 + \bar{S}_2 + \bar{S}_3. \quad (1)$$

Here  $\bar{S}_1$  represents the vibrational contribution,  $\bar{S}_2$  the electronic term, and  $\bar{S}_3$  the degeneracy term. This last term is equal to zero when there is only one interstitial site available per metal atom.

$\bar{S}_1$  may be divided into two parts (12):  $\bar{S}_1(H)$ , which arises from vibration of the hydrogen atoms proper, and  $\bar{S}_1(M)$ , which is due to the modification of the vibrational spectrum of the solvent metal, M. It is expected that  $\bar{S}_1(H)$  may be calculated to a good approximation from the Einstein model.

In Table I we summarize experimental values of the excess entropy (6, 12-15) for dilute solutions of hydrogen in palladium and compare the results with calculated values. The special difficulties which arise from the existence of two different localized modes in

bcc metals (16, 17) are not present in fcc metals such as palladium.

$\bar{S}_1(H)$  has been calculated from the neutron scattering data of Drexel *et al.* (18). While  $\bar{S}_1(M)$  is a rather complicated term to evaluate, the existence of such a term has been recognized for a long time (19). Some years ago Wagner (20) proposed to calculate this term by considering only the thermal expansion of the lattice. Relating this macroscopic approach to an earlier microscopic study of point defects by Huntington *et al.* (21), Boureau *et al.* (12) showed that Wagner's method overestimates  $\bar{S}_1(M)$ . The same conclusion was reached by Magerl *et al.* (7) on the basis of elasticity calculations (22) and taking into account also electron-phonon interactions.

In order to evaluate  $\bar{S}_1(M)$ , low-temperature calorimetric (23, 24) and neutron scattering data (25) have been used (6). Contrary to suggestions made in earlier studies (6, 7, 26, 27), Rowe (28) recently has shown that these two methods are in reasonable agreement. From the calculations of Rowe, we estimate  $\bar{S}_1(M)$  for hydrogen in palladium to be about  $+0.2 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$ .

$\bar{S}_2$  may be calculated from low-temperature heat capacity data by taking into account the change of the electronic heat capacity coefficient  $\gamma$  with temperature, as determined for pure Pd by Müller and Brockhouse (29). In Table I,  $\bar{S}_2$  has been obtained in this way by assuming that  $\bar{S}_2$  is the same in the

TABLE I  
COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF THE  
PARTIAL MOLAR EXCESS ENTROPY OF HYDROGEN IN PALLADIUM AT  
DIFFERENT TEMPERATURES<sup>a</sup>

Temperature	Refs.	$\bar{S}_1(H)$	$\bar{S}_1(M)$	$\bar{S}_2$	$\bar{S}_H^E(\text{calc})$	$\bar{S}_H^E(\text{exp})$	$\bar{S}_H^E(\text{exp}) - \bar{S}_H^E(\text{calc})$
300	(13-15)	1.6	0.2	-0.6	1.2	2.8	1.6
500	(6, 12, 15)	3.8	0.2	-0.9	3.1	5.3	2.2
700	(6)	5.5	0.2	-1.1	4.6	7.6	3.0

<sup>a</sup> Data in  $\text{cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$ . Details of the calculation are presented in the text.

$\alpha$ -phase and at the lowest hydrogen content in the  $\beta$ -phase. Our values are about 25% less negative than those given by Oates and Flanagan (30), who based their estimate on the rigid band approximation.

Neutron scattering experiments (31–33) indicate that at least up to 700°K only octahedral interstitial sites are occupied by hydrogen in palladium. This conclusion is consistent with the recent observation that the diffusion mechanism seems to be the same for hydrogen in  $\alpha$ -Pd and in  $\beta$ -Pd (34), and also with the band theory calculations of Sholls and Smith (35). Although a slight degeneracy is enough to create a significant contribution to  $\bar{S}_H^E$  (36), it is evident that  $\bar{S}_3$  cannot be very large. It is apparent from the data listed in Table I that even at room temperature the calculated values of  $\bar{S}_H^E$  are much smaller than the experimental values. Furthermore, the magnitude of the discrepancy increases with increasing temperature.

### III. The Einstein Model

Dilute solutions of hydrogen in metals are among the several solid state examples where the Einstein model of atomic vibrations might be expected to hold: The hydrogen atoms are located on well-separated interstitial sites and interact only weakly with each other. Moreover, the localized optical modes of the hydrogen atoms have frequencies well outside the acoustic band of the host metal. An additional favorable aspect of solutions of hydrogen in fcc metals is the expected isotropic character of the hydrogen vibrations referred to in Section II above. Therefore the assumption of a single vibrational frequency seems quite plausible.

The partition function of an Einstein oscillator is given by (37)

$$z = \frac{\exp(-h\nu/kT)}{1 - \exp(-h\nu/kT)}. \quad (2)$$

From this relation we may readily calculate the experimental quantities  $\delta\Delta\bar{G} = \Delta\bar{G}_D - \Delta\bar{G}_H$ ,  $\delta\Delta\bar{H} = \Delta\bar{H}_D - \Delta\bar{H}_H$ , and  $\delta\bar{S}^E = \bar{S}_D^E - \bar{S}_H^E$ , i.e., the differences between the partial molar free energy, the partial molar enthalpy, and the partial molar excess entropy of hydrogen and of deuterium, respectively. These quantities are expressed as functions of the hydrogen and deuterium frequencies,  $\nu_H$  resp.  $\nu_D$ , by the relations:

$$\begin{aligned} \delta\Delta\bar{G} = \Delta U_0 + \frac{1}{2} \int_0^T [C_p(H_2) - C_p(D_2)] dT \\ + \frac{3}{2} Nh(\nu_D - \nu_H) \\ + 3RT \ln \frac{1 - \exp(-h\nu_D/kT)}{1 - \exp(-h\nu_H/kT)} \\ - \frac{1}{2} T[S(H_2) - S(D_2)], \end{aligned} \quad (3)$$

$$\begin{aligned} \delta\Delta\bar{H} = \Delta U_0 + \frac{1}{2} \int_0^T [C_p(H_2) - C_p(D_2)] dT \\ + \frac{3}{2} Nh(\nu_D - \nu_H) + 3N \\ \times \left[ \frac{h\nu_D}{\exp(h\nu_D/kT) - 1} \right. \\ \left. - \frac{h\nu_H}{\exp(h\nu_H/kT) - 1} \right], \end{aligned} \quad (4)$$

$$\begin{aligned} \delta\bar{S}^E = -3R \ln \left[ \frac{1 - \exp(-h\nu_D/kT)}{1 - \exp(-h\nu_H/kT)} + \frac{h\nu_D}{T} \right. \\ \times \frac{1}{\exp(h\nu_D/kT) - 1} \\ \left. - \frac{h\nu_H}{T} \times \frac{1}{\exp(h\nu_H/kT) - 1} \right], \end{aligned} \quad (5)$$

$$\nu_H/\nu_D = 2^{1/2}. \quad (6)$$

Here  $\Delta U_0$  is one-half of the difference of the dissociation energies of gaseous molecules of  $H_2$  and  $D_2$  at 0°K. According to JANAF (33),  $\Delta U_0$  is 901 cal mole<sup>-1</sup>.

Relations (2)–(5) have been used for a long time to calculate the vibrational frequency of

TABLE II  
VIBRATIONAL FREQUENCIES (IN  $\text{cm}^{-1}$ ) FOR HYDROGEN IN PALLADIUM AND IN  
PALLADIUM-SILVER ALLOYS FROM THERMODYNAMIC MEASUREMENTS AND  
FROM NEUTRON SCATTERING EXPERIMENTS

References <sup>a</sup>	Solvent	$\tilde{\nu}_H$				Neutron scattering value
		Temperature (°K)	$\Delta\bar{S}_D - \Delta\bar{S}_H$	$\Delta\bar{H}_D - \Delta\bar{H}_H$	$\Delta\bar{G}_D - \Delta\bar{G}_H$	
(12)	Pd	555	635	698	746	552
(39)	Pd <sub>0.9</sub> Ag <sub>0.1</sub>	390	—	—	757	565
(10)	Pd <sub>0.9</sub> Ag <sub>0.1</sub>	555	640	723	804	565
(10)	Pd <sub>0.9</sub> Ag <sub>0.1</sub>	700	690	783	847	565

<sup>a</sup> Thermodynamic measurements.

hydrogen (see, for instance, Ref. (5)). In a recent study (10) we have applied these relations to experimental data for solutions of hydrogen and deuterium in palladium (12) and in the alloy Pd<sub>0.9</sub>Ag<sub>0.1</sub> (10, 39), and have compared the results with frequencies deduced from neutron scattering work (18, 40, 41). The data are shown in Table II. The essential features are:

1. All vibrational frequencies calculated from thermodynamic data are larger than those derived from inelastic neutron scattering.

2. In all cases there is a definite increase of the thermodynamically calculated frequencies with increasing temperature.

3. There are systematic discrepancies between the calculated values of  $\nu_{\Delta\bar{S}}$ ,  $\nu_{\Delta\bar{H}}$ , and  $\nu_{\Delta\bar{G}}$ , i.e., the frequencies derived from comparisons between the partial molar entropies, the partial molar enthalpies, and the partial molar Gibbs free energies of solution. In all cases, we find  $\nu_{\Delta\bar{G}} > \nu_{\Delta\bar{H}} > \nu_{\Delta\bar{S}}$ . As is apparent from Table III, the Einstein model provides a better prediction of  $\delta\bar{S}^E$  than of  $\delta\Delta\bar{H}$ .

TABLE III  
COMPARISON OF EXPERIMENTAL PARTIAL MOLAR QUANTITIES FOR HYDROGEN IN PALLADIUM  
AND IN Pd<sub>0.9</sub>Ag<sub>0.1</sub> WITH VALUES CALCULATED FROM SOME SIMPLE MODELS<sup>a</sup>

	$\Delta\bar{H}_D - \Delta\bar{H}_H$			$\bar{S}_D^E - \bar{S}_H^E$			$\Delta\bar{G}_D - \Delta\bar{G}_H$		
	Pd		Pd <sub>0.9</sub> Ag <sub>0.1</sub>	Pd		Pd <sub>0.9</sub> Ag <sub>0.1</sub>	Pd		Pd <sub>0.9</sub> Ag <sub>0.1</sub>
	555°K	555°K	700°K	555°K	555°K	700°K	555°K	555°K	700°K
Experimental value	470	440	455	1.76	1.77	1.83	448	408	387
Einstein model $\nu_H/\nu_D = 2^{1/2}$	619	598	644	1.83	1.81	1.90	557	546	522
Einstein model $\nu_H/\nu_D = 1.53$	579	554	609	2.26	2.24	2.35	276	263	176
Free particle model	888	888	879	2.06	2.06	2.06	699	699	648
Oates and Flanagan treatment	545			1.97			406		

<sup>a</sup>  $\Delta\bar{H}_D - \Delta\bar{H}_H$  and  $\Delta\bar{G}_D - \Delta\bar{G}_H$  are, respectively, the differences in partial molar enthalpies and Gibbs free energies of deuterium and of hydrogen (in cal mole<sup>-1</sup>).  $\bar{S}_D^E - \bar{S}_H^E$  is the corresponding difference of the partial molar excess entropies (in cal mole<sup>-1</sup>°K<sup>-1</sup>). These quantities have been calculated using the Einstein frequency  $\tilde{\nu}_H = 552 \text{ cm}^{-1}$  for hydrogen in pure palladium, and  $\nu_H = 565 \text{ cm}^{-1}$  for hydrogen in Pd<sub>0.9</sub>Ag<sub>0.1</sub>. The experimental data are taken from Refs. (10, 12).

The two first features of these results were noted already by Oates and Flanagan (9), who showed that for solutions of hydrogen in palladium,  $\nu_{\Delta\bar{G}}$  increases significantly from room temperature to 1300°K.

#### IV. Transition Towards A Fluid State

##### A. The Use of the Concept of Communal Entropy

Kleppa *et al.* (42) proposed the use of the concept of "communal entropy" (43, 44) in order to describe the thermodynamic behavior of hydrogen in metallic solutions at high temperatures. In this representation the hydrogen atoms are still basically considered as localized Einstein oscillators, but they acquire an additional entropy of  $R$  per mole through the removal of restrictions on their movement. Boureau and Kleppa (6) suggested that the increase of the partial molar excess entropy of hydrogen in palladium between 300 and 700°K may be explained through such a progressive acquisition of communal entropy.

In fact, this point of view is not correct since the communal entropy has been shown to be caused not by the delocalization of the atoms but by the restriction of having a single atom per cell (45). Since in metal-hydrogen systems this restriction remains valid even at high temperature, it is evident that the concept of communal entropy is not appropriate.

##### B. The Approach of T. Hill

Hill studied the problem of the hindered translation of atoms on a surface (43, 46), and proposed the existence of three different temperature ranges for solutions of hydrogen in metals: (1) a localized oscillator state at low temperature, (2) a transition region at intermediate temperatures, and (3) a free particle state at high temperatures. We shall comment briefly on this approach which

in various forms has been adopted in several recent studies (9, 47, 48):

1. Hill predicts a heat capacity maximum at  $T = V_0/R$ , where  $V_0$  is the potential barrier between two sites. If  $V_0$  is identified with the activation energy for diffusion, such a maximum should be observed near  $T = 550^\circ\text{K}$ . This seems to be in fair agreement with the observations of Boureau and Kleppa (6), who found large values of  $\bar{C}_p(\text{H})$  near 700°K.

2. In spite of the fact that most of the volume of the metal is occupied by the metallic ions, it is well known that the number density of hydrogen atoms in hydrides is larger than in the liquid state (49). Moreover, a typical diffusion coefficient for hydrogen in a metal is about  $10^{-4}$  to  $10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ . This compares with values of the order of  $1 \text{ cm}^2 \text{ sec}^{-1}$  for a gas. Thus, the assumption that hydrogen in a metal at high temperature behaves somewhat like a perfect monatomic gas certainly is not correct.

3. Recent neutron scattering studies (31, 32) indicate that even at 700°K the time interval between two atomic jumps in the Pd-H<sub>2</sub> system ( $\sim 1.5 \times 10^{-12} \text{ sec}$ ) is much longer than the vibrational period ( $\sim 6 \times 10^{-14} \text{ sec}$ ). Therefore, even if the assumption of a large fluid-like contribution to the entropy is accepted, it is not due to a gas-like motion of the atoms throughout the whole lattice.

4. McLellan (48) attempted to apply the method proposed by Hill to describe hydrogen dissolved in vanadium, niobium, and tantalum at 500°K. Actually, he considered only the high-temperature limit, and his model is very similar to the classical Sackur-Tetrode treatment (50-52) of a monatomic gas with some assumptions regarding the volume available to the hydrogen atoms.

If we use the Sackur-Tetrode treatment to describe the free particle state, Eqs. (3)-(5) become simply:

$$\delta\Delta\bar{G} = \Delta U_0 + \frac{1}{2} \int_0^T [C_p(\text{H}_2) - C_p(\text{D}_2)] dT - \frac{3}{2} RT \ln 2 + \frac{1}{2} T [S(\text{H}_2) - S(\text{D}_2)], \quad (7)$$

$$\delta\Delta\bar{H} = \Delta U_0 + \frac{1}{2} \int_0^T [C_p(\text{H}_2) - C_p(\text{D}_2)] dT, \quad (8)$$

$$\delta\bar{S}^E = \frac{3}{2} R \ln 2. \quad (9)$$

If these results are applied to tantalum-hydrogen and tantalum-deuterium at 700°K and compared with the recent experimental data for these systems of Dantzer and Kleppa (53), it is immediately apparent that the free particle model fails. This model would imply  $\Delta\bar{H}_D - \Delta\bar{H}_H = 878 \text{ cal mole}^{-1}$  and  $\bar{S}_D^E - \bar{S}_H^E = 2.06 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$ . In fact the experimental differences are  $-220 \text{ cal mole}^{-1}$  and  $1.40 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$ , respectively. Similar discrepancies are found for Pd-H<sub>2</sub> (see Table III). Clearly the free particle model is inappropriate for this system at 700°K.

### V. Failure of the Born-Oppenheimer Approximation in the Palladium-Hydrogen System

One way of improving the agreement between the thermodynamic determinations of  $\nu_H$  and the neutron scattering data is to relax the condition  $\nu_H/\nu_D = 2^{1/2}$ . This finds support in the following observations:

1. The 4°K tunneling experiments of Dynes and Garno (54) are consistent with a ratio  $\nu_H/\nu_D$  of about 1.5.

2. The theoretical analysis of the inverse isotope effect by Ganguly (55-58) also is based on the assumption that this ratio is larger than  $2^{1/2}$ .

3. The lattice dynamics analysis of hydrogen (deuterium) in palladium ( $\beta$ -phase) by Rahman *et al.* (59) indicates that the force constant is about 20% larger for hydrogen than for deuterium.

On the basis of these considerations, Boureau *et al.* (12) set  $\nu_H/\nu_D = 1.5$  in order to fit their thermodynamic data. More recently, Oates and Flanagan (9) have used  $\nu_H/\nu_D = 1.53$ . Actually, as may be seen from Table III, the latter value does not provide a better agreement. This was recognized by Oates and Flanagan, who, as already mentioned, proposed to eliminate the discrepancy by assuming a soft transition for the hydrogen (deuterium) atoms from a localized oscillator state at low temperature to a free particle state at high temperature.

Several objections may be made to this approach:

1. The experimental observation of a ratio  $\nu_H/\nu_D$  much larger than  $2^{1/2}$  also may be explained by assuming a hard potential well. In this case, the thermodynamic treatment would be quite different.

2. It seems that, as far as well-localized excitations are concerned, the neutron scattering data so far available (18) do not support a ratio  $\nu_H/\nu_D$  much larger than about  $2^{1/2}$  for  $\alpha$  solid solutions. Hence, a force constant 15-20% larger for hydrogen than for deuterium does not seem realistic. Moreover, very recent calculations (60) show that such a marked breakdown of the Born-Oppenheimer approximation in dilute solutions is unlikely.

3. As is apparent from Table III, the use of a ratio  $\nu_H/\nu_D$  significantly larger than  $2^{1/2}$  actually gives rise to higher values of  $\delta\bar{S}^E$ , whereas the experimental values are lower than those calculated from the Einstein model.

4. With respect to the treatment of Oates and Flanagan, we have already indicated above that doubts may be raised about its validity. Let us now mention another point: The Oates-Flanagan model predicts a larger value of  $\delta\bar{S}^E$  than the Einstein model, whereas the experimental data actually are lower. This discrepancy is "hidden" by the prediction of a value of  $\delta\Delta\bar{H}$  smaller than that calculated by the Einstein model, which

allows the model to provide a fair agreement for  $\delta\Delta\bar{G}$ . This was the only thermodynamic quantity considered by Oates and Flanagan.

## VI. The Anharmonic Oscillator

### A. Use of a Soft Potential Well

The usual simple treatment of high-temperature anharmonicity in crystals (61) assumes that the potential well in which the considered atom finds itself flattens in the directions in which there is a saddle point. Hence the spacing between two consecutive energy levels would decrease as the energy increases. This effect, if it were present, in large measure would explain the high values of  $\bar{S}_H^E$  at high temperature. In fact, Magerl *et al.* (7) recently have suggested an explanation along these lines. However, our own calculations show that as a result, we would also expect to observe values of  $\bar{S}_D^E - \bar{S}_H^E$  slightly larger and values of  $\Delta\bar{H}_D - \Delta\bar{H}_H$  much larger than those calculated from the simple Einstein model. In fact, if such a potential were present, we would predict  $\nu_{\Delta\bar{S}} > \nu_{\Delta\bar{H}} > \nu_{\bar{G}}$ . For hydrogen in palladium this is contrary to the experimental observations. We also find it difficult to invoke this effect in order to explain the large value of  $\bar{S}_H(\text{measured}) - \bar{S}_H(\text{calculated})$  at the low temperature of 300°K (see Table I).

### B. The Use of a Hard Potential Well

Katz *et al.* (62) concluded that their measurements of the diffusion coefficients of hydrogen, deuterium, and tritium in nickel could not be fitted by assuming a single Einstein frequency. In order to avoid the use of a temperature-dependent vibrational frequency, they proposed the existence of a hard potential well, the justification of which is the assumption of a strong repulsion between the screened protons and the ion cores of the metal.

The principal difficulty with the model of Katz *et al.* is that it cannot be reconciled with

the neutron scattering studies and with the experimental determinations of  $\bar{S}_H^E$ :

1. According to Drexel *et al.* (18), the motion of the protons may be approximated as harmonic oscillations in the [100] direction, i.e., in the direction in which strong repulsive anharmonic effects are to be expected from the model of Katz *et al.*

2. The experimental determination of the two first harmonics by neutron scattering (18) is not consistent with the assumption of a large difference between the two first energy level spacings as predicted by the model of Katz *et al.*

3. A direct consequence of the adoption of hard well potential would be a reduction of the excess entropy, which makes it still more difficult to decompose it into different contributions.

## VII. A Qualitative Representation

Since we lack information on the interatomic forces between the hydrogen atoms and their host metal atoms (63), only a qualitative treatment is possible. We propose to explain the large values of  $\bar{S}_H^E$  observed in the Pd-H<sub>2</sub> system (see Table I), and probably also present in other metal-hydrogen systems such as Ta-H<sub>2</sub> (53), by considering the hydrogen atoms as intermediate between two representations: (i) Einstein oscillators, and (ii) Particles constrained to move only within a cell. The latter representation is equivalent to single-occupancy systems such as those defined by Hoover and Ree (64, 65), in order to study the melting transition. Following Ree (65), the entropy, in this representation, will be equal to:

$$\bar{S}_H = S(\text{H gas}) - R \ln \frac{V(\text{H})}{V_H(\text{Pd})} - S^e(\text{Padé}) - \Delta S(\text{communal}). \quad (10)$$

In this expression,  $S(\text{H})$  is the standard entropy of hydrogen gas (H), such as may be found in the JANAF tables,  $V(\text{H})$  the normal volume of hydrogen,  $S^e(\text{Padé})$  the

term calculated for a hard sphere fluid by Hoover and Ree, and  $\Delta S(\text{communal})$  the communal entropy caused by the constraint of having only one interstitial hydrogen atom per interstitial site.

The numerical value of  $\bar{S}_H$  depends very strongly on the actual values chosen for  $V_H(\text{Pd})$  and for the volume of the hydrogen hard spheres. Both of these terms are somewhat arbitrary. With  $V_H(\text{Pd}) = 1.8 \text{ cm}^3 \text{ mole}^{-1}$  and  $V(\text{hard sphere}) = 0.4 \text{ cm}^3 \text{ mole}^{-1}$ , we calculate a value of  $\bar{S}_H$  of  $7 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$  at  $300^\circ\text{K}$ . This result should be compared with  $S_1(\text{H}) = 1.6 \text{ cal mole}^{-1} \text{ }^\circ\text{K}^{-1}$  in Table I. It is evident that we may explain the large value of  $\bar{S}_H^E$  by assuming an intermediate state. This interpretation also seems to be consistent with the large anharmonic effect observed (18) for dilute solutions of hydrogen in palladium.

It is of interest to note that the assumption of a liquid-like character of hydrogen does not imply a modification of the configurational entropy term  $R \ln[(1-x)/x]$ . In this respect our representation differs from models based on the approach of Hill (9, 46-48).

On the other hand, we believe that the assumption of a force constant slightly larger for hydrogen than for deuterium (perhaps about 5%) is justified. We note, in particular, that this assumption is consistent with a well-known anomaly: Below  $500^\circ\text{K}$  deuterium is known to diffuse faster than hydrogen in palladium (66, 67). This may be explained by the classical theory of diffusion (68, 69) if the existence of a saddle point with an adjustable Einstein frequency is accepted (70). However, this point of view recently has been criticized (71, 72). While the origin of the effect is not known, let us advance a hypothesis: The motion of the screened proton in the [110] direction tends to weaken the metallic cohesion. Because of the large effective mass of the  $d$  electron in this direction (73, 74), the repulsive force may well

increase with the speed of the proton and have the character of a frictional force.

We shall now outline how our qualitative representation possibly may explain observed differences between solutions of hydrogen in bcc and fcc metals (see also Table IV).

In fcc metals, all factors contribute to reduce  $\delta\Delta\bar{H}$ , whereas the expected stronger repulsion of hydrogen atoms than of deuterium atoms contributes to an increase of  $\delta\bar{S}^E$ . The net result will be a strong decrease of  $\delta\Delta\bar{H}$  and a moderate decrease of  $\delta\bar{S}^E$  compared to the values calculated from the Einstein model. On the other hand, from relations (3) to (5) one finds that, at least for temperatures not too high,  $\delta\Delta\bar{H}$  and  $\delta\bar{S}^E$  both decrease as the frequency increases. Hence, as may be expected, and this is confirmed by calculations for solutions in nickel, palladium, and  $\text{Pd}_{0.9}\text{Ag}_{0.1}$ , we have

$$\nu_{\Delta\bar{H}} > \nu_{\Delta\bar{S}}$$

TABLE IV  
COMPARISON OF DIFFERENT ESTIMATED CONTRIBUTIONS TO  $\delta\Delta\bar{H}$  and  $\delta\bar{S}^E$  HYDROGEN IN fcc AND bcc METALS<sup>a</sup>

A. fcc metals			
	Larger force constant for H	Fluid-like character more marked for H	Total
$\delta\Delta\bar{H}$	-	-	-
$\delta\bar{S}^E$	+	-	?
B. bcc metals			
	Soft well	Fluid-like character more marked for H	Total
$\delta\Delta\bar{H}$	+	-	?
$\delta\bar{S}^E$	+	-	?

<sup>a</sup> +, An increase of  $\delta\Delta\bar{H}$  or  $\delta\bar{S}^E$ ; -, a decrease compared to the Einstein model.



(i.e., the frequency calculated from  $\delta\Delta\bar{H}$  is larger than the frequency calculated from  $\delta\bar{S}^E$ ).

Accordingly

$$\begin{aligned} \delta\Delta\bar{H}(\nu_{\Delta\bar{H}}) - T\delta\Delta\bar{S}(\nu_{\Delta\bar{H}}) \\ > \delta\Delta\bar{H}(\nu_{\Delta\bar{H}}) - T\delta\Delta\bar{S}(\nu_{\Delta\bar{S}}). \end{aligned}$$

The right-hand side of this inequality is equal to  $\delta\Delta\bar{G}(\nu_{\Delta\bar{G}})$ . Hence

$$\nu_{\Delta\bar{G}} > \nu_{\Delta\bar{H}} > \nu_{\Delta\bar{S}}.$$

Moreover, detailed calculations show that a small increase of  $\nu_{\Delta\bar{H}} - \nu_{\Delta\bar{S}}$  gives rise to a large increase of  $\nu_{\Delta\bar{G}}$ . For this reason,  $\nu_{\Delta\bar{G}}$  is a less meaningful quantity than  $\nu_{\Delta\bar{H}}$  and  $\nu_{\Delta\bar{S}}$ ; i.e., the calculation of  $\nu_{\Delta\bar{G}}$  amplifies the discrepancy between  $\nu_{\Delta\bar{H}}$  and  $\nu_{\Delta\bar{S}}$ . This is of some importance because  $\delta\Delta\bar{G}$  frequently has been used to calculate  $\nu$  (9, 75).

For bcc metals, as may be seen from Table IV, it is not immediately clear if  $\delta\bar{S}^E$  and  $\delta\Delta\bar{H}$  will be smaller or larger than the values calculated from the Einstein model:

1. There is still a fluid-like entropy term, as is confirmed by the recent work of Dantzer and Kleppa (53). This term will contribute to the decrease of both  $\delta\Delta\bar{H}$  and  $\delta\bar{S}^E$ .

2. The potential is not harmonic but flattens in the diffusion direction [100]. This will give rise to a moderate increase of  $\delta\bar{S}^E$  and a strong increase of  $\delta\Delta\bar{H}$ .

3. As already mentioned, two different frequencies are expected in bcc metals. The intensity of the higher frequency, observed in the [100] direction, increases with increasing temperature. This will give rise to a decrease of both  $\delta\bar{S}^E$  and of  $\delta\Delta\bar{H}$ .

Since the perturbing factors work in different directions, it is difficult to predict the overall result. However, for systems with a very low activation energy for diffusion, it would be expected that the influence of the soft well potential should be predominant. This seems indeed to be the case:

From the equilibrium data of Steward (75) for hydrogen and deuterium in niobium, we calculate at about 650°K,  $\tilde{\nu}_{\Delta S} = 1680 \text{ cm}^{-1}$ ,

$\tilde{\nu}_{\Delta H} = 1475 \text{ cm}^{-1}$ , and  $\tilde{\nu}_{\Delta G} = 1250 \text{ cm}^{-1}$ . Moreover,  $\tilde{\nu}_{\Delta G}$  decreases as the temperature increases.

On the other hand, for solutions in tantalum, in which the activation energy for diffusion is larger, the different terms seem to cancel: Dantzer and Kleppa (53) find  $\tilde{\nu}_{\Delta H} \approx \tilde{\nu}_{\Delta S} \approx \tilde{\nu}_{\Delta G} \approx 1350 \text{ cm}^{-1}$  at 715°K. This result is in good agreement with the determination of  $\tilde{\nu}_{\Delta G}$  at 400°K made by Steward (75) based on the equilibrium measurements of Pryde and Tsong (76). Even so, we believe that it would be erroneous to conclude from this that hydrogen atoms in tantalum may be described as isotropic harmonic oscillators.

## Summary and Conclusions

In this paper we have attempted to improve our understanding of the thermodynamics of the solutions of hydrogen and deuterium in metals and have shown that the previously advanced models are missing significant points. The following conclusions have been reached:

1. Generally, the description of the hydrogen atoms in dilute metallic solutions as simple harmonic oscillators represents only a crude first approximation. Even so, in cases where reliable neutron scattering data are not available, the Einstein model may be used to obtain an approximate value of the vibrational frequency. In calculating  $\nu_H$  and  $\nu_D$ , it is desirable to use the differences between the partial molar entropies of hydrogen and deuterium rather than the difference between the Gibbs free energies.

2. The most acceptable explanation for the difference between the calculated and measured partial entropies of hydrogen is the existence of a liquid-like entropy contribution; the importance of this term increases with increasing temperatures. Even at high temperatures the lattice configurational entropy term ( $R\ln[(1-x)/x]$ ) remains present.

3. For dilute solutions in fcc metals such as palladium the assumption of a force constant slightly larger for hydrogen than for deuterium seems consistent with the available diffusion data. It also provides a plausible explanation for the difference between solutions of hydrogen in fcc and bcc metals.

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