

High-Temperature Thermodynamics of Dilute Solutions of Hydrogen and Deuterium in Tantalum and in Dilute Tantalum-Oxygen Solid Solutions

P. G. DANTZER* AND O. J. KLEPPA†

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

Received July 5, 1977

We report a comparison between the partial enthalpies of solution of hydrogen ($\Delta\bar{H}_H$) and of deuterium ($\Delta\bar{H}_D$) in tantalum at 715°K and find $\Delta\bar{H}_D - \Delta\bar{H}_H = -220$ cal mole⁻¹. This allows a calculation of the average vibrational frequency of hydrogen which is 1350 cm⁻¹. On the basis of this result we have made a new estimate of the "residual" excess entropy ($\bar{S}_H^E - \bar{S}_H(\text{vibr}) - \bar{S}_H(\text{el})$) for hydrogen and deuterium and find a value of 4.6 cal °K⁻¹ mole⁻¹. This is consistent with occupancy by hydrogen of the tetrahedral interstitial sites, and may possibly reflect occupancy of both tetrahedral and octahedral sites. The presence of oxygen in solid solution in tantalum in amounts of 1-3 at.% makes the partial enthalpy of solution more negative, and also reduces the partial entropy by about 1 cal °K⁻¹ mole⁻¹. The net effect of these two terms is to increase the partial pressure of hydrogen compared to pure tantalum at low oxygen contents, but to reduce the partial pressure at higher oxygen contents ($N_O \gtrsim 0.03$).

Introduction

In recent communications we have published detailed calorimetric and equilibrium data for the solid solutions of hydrogen in bcc V, Nb, and Ta (1, 2). In this work we reported new information on the dependence of the partial enthalpy of solution of hydrogen on temperature, and we attempted to explain the observed values of the excess entropy of hydrogen in terms of vibrational, electronic, volume change, and degeneracy contributions in the manner originally proposed by O'Keefe and Stewart (3).

In our previous calculation of the vibrational entropy of hydrogen in tantalum we based our estimate on an assumed vibrational frequency of 970 ± 50 cm⁻¹, taken from the

neutron-scattering work on V-H alloys of Rush and Flotow (4). In the present work we have measured the partial enthalpies of solution of hydrogen and deuterium in tantalum. This allows us to calculate directly a new average vibrational frequency of hydrogen, and to obtain a revised value of the vibrational entropy of hydrogen.

A second objective of the present investigation has been the measurement of the partial enthalpy of solution of hydrogen in "pure" (i.e., as received) tantalum, and in tantalum metal which contained known amounts of oxygen in solid solution. While there have been many thermodynamic investigations of binary metal-hydrogen alloys, we have found very little information in the literature on the thermodynamics of ternary metal-hydrogen-oxygen systems. The present communication represents a modest first exploration in this general area. We propose to

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

† Author to whom correspondence is to be addressed.

give further attention to this problem in future work.

Finally, a third objective of the present work has been to obtain additional information on the fairly reproducible but so far unexplained anomalies in the observed partial enthalpies and excess entropies of hydrogen in very dilute solutions in tantalum. We observed these anomalies in our earlier work (1, 2), and somewhat similar behavior had previously been reported in equilibrium studies by Kofstad *et al.* (5), Katz and Gulbransen (6), Veleckis and Edwards (7), and McQuillan and Wallbank (8).

It is not as yet clear to what extent these anomalies might have been caused by the thermal transpiration effect recently discussed by Wallbank and McQuillan (9). However, it was suggested by Kofstad *et al.*, that the anomalies might perhaps be related to the presence in the metal of interstitial impurities such as oxygen, nitrogen, and carbon. In fact, these authors found that the effect was somewhat enhanced in experiments on tantalum which contained 0.56 at.% oxygen. We hoped that our own experiments with oxygen-containing alloys might throw some further light on this problem.

Experimental and Materials

Most of our measurements were carried out at 713–716°K using the same gas-measuring system and the same Calvet-type twin calorimeter as in our earlier work. However, for a series of measurements at 876°K we substituted a single unit microcalorimeter suitable for the higher temperature.

The tantalum metal was again in the form of 0.005-cm thick foil purchased from Fansteel. However, our sample was taken from a different batch of material. A typical analysis is given in Ref. (1). Prior to use the foil was cut into strips 0.5 cm wide \times 7 cm long, degreased in trichlorethylene, and then washed first in acetone and finally in absolute alcohol.

In our study of the solutions of hydrogen and deuterium in "pure" tantalum, a weighed amount of metal was either enclosed in an 8-cm-long protective stainless steel crucible (to avoid contamination by reaction with the fused silica wall, Series 1a, 1b), or the foil was placed directly into the fused silica "liner" (Series 2, 3, 4). (Runs labeled by the same serial number used the same weighed-in sample of tantalum. For series denoted by letters, i.e., 1a, 1b, etc., hydrogen was completely desorbed from the sample between runs a and b.)

The alloys of tantalum and oxygen were prepared by dissolving known amounts of oxygen gas in pure tantalum. This process was carried out in the fused silica liner, initiated by heating the liner containing metal and gas at the rate of about 50° per hour from 200 to 600°C. At this temperature the initial volume of oxygen gas had been completely absorbed. Finally, the foils were annealed for three days at 950°C in order to ensure homogenization of the sample. The oxygen contents of the alloys were checked by the gains in weight, and agreed with the calculated amounts. The following alloy compositions were used: Series 2: Ta, 0.92 at.% O; Series 3: Ta, 2.97 at.% O. For these alloy samples we did not use any protective stainless steel crucible between sample and silica liner. However, we prevented direct contact between liner and sample by means of a small silica container.

The hydrogen and deuterium gases were purified by absorption in and desorption from titanium powder. The deuterium gas was purchased from Union Carbide (c.p., ~99.5% D₂). As received the tantalum foils react very sluggishly with hydrogen at 700°K. In order to obtain acceptable reaction rates the foils were placed in the fused silica liner, and then "activated" in a separate furnace by absorbing and desorbing purified hydrogen at about 550°C. This process was repeated four to six times until absorption was essentially instantaneous. The liner was then evacuated to a pressure of about 10⁻⁶ Torr while the temperature was raised to 640°C (Series 1 only)

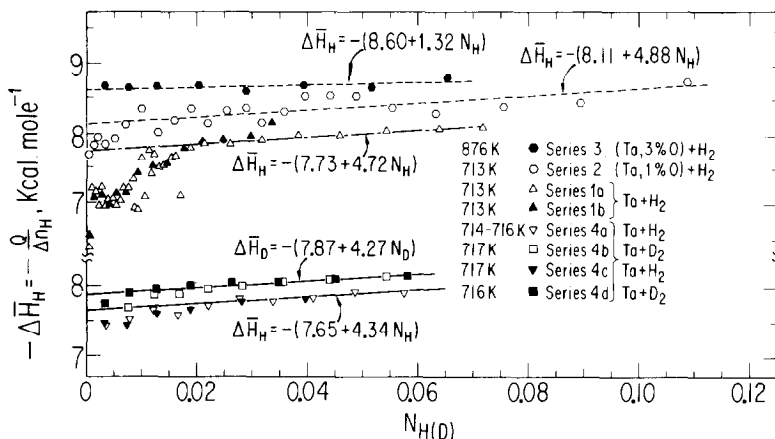


FIG. 1. Partial enthalpies of solution of hydrogen and of deuterium in tantalum and in tantalum–oxygen solid solutions at indicated temperatures plotted against mole fraction of H(D).

or 850°C (all other Series). The sample was maintained at this temperature for about 12 hr before the liner was introduced into the calorimeter.

In order to obtain reasonable heat effects (0.5 cal or larger) and reliable results in the dilute solution range, we used quite large samples of tantalum metal (about 20 g). This has the consequence that for higher hydrogen contents (mole fraction, $N_H \gtrsim 0.06$) the amount of gas necessary to produce a significant change in mole fraction becomes quite large. Also, the time required to reach equilibrium is longer (> 1 hr), and there is a tendency to underestimate the heat of reaction by perhaps 1 to 2%.

Results and Discussion

The observed partial molar enthalpies of solution of hydrogen are shown graphically in Fig. 1. In comparing our new enthalpy data with our earlier results it should be noted that in our earlier work we incorrectly identified the observed heat effects as changes in *internal energy* rather than in *enthalpy* (10). Hence, the previously published enthalpy data are too negative by a term $\frac{1}{2}RT$.

Figure 1 shows that for values of N_H larger than about 0.02 there is very good agreement between the results obtained in Series 1a, 1b (pretreated at 640°C) and Series 4a, 4c (pretreated at 850°C). By extrapolating the high-concentration data linearly to $N_H = 0$, we find for these two series the limiting values of $\Delta\bar{H}_H$ at 713–716°K of -7.73 and -7.65 kcal mole $^{-1}$, respectively. The corresponding value at 703°K taken from Ref. (1) (corrected by $\frac{1}{2}RT$) is -7.80 kcal mole $^{-1}$.

The Isotope Effect

In order to obtain the best possible value for the difference between the enthalpies of solution of hydrogen and of deuterium we carried out four consecutive series of calorimetric measurement on the same metal sample at about 715°K: [4a (Ta + H₂); 4b (Ta + D₂); 4c (Ta + H₂); 4d (Ta + D₂)]. The data plotted in Fig. 1 show that there is excellent agreement between the enthalpies measured in Series 4a and 4c on the one hand, and in Series 4b and 4d on the other. We find

$$\Delta\bar{H}_D - \Delta\bar{H}_H = -220 \text{ cal mole}^{-1}$$

with an estimated uncertainty of about ± 25 cal

mole⁻¹. This difference applies at all concentrations up to about $N_{\text{H(D)}} \approx 0.06$.

It is generally assumed that hydrogen and deuterium dissolved interstitially in metals such as tantalum may be considered as independent, three-dimensional Einstein oscillators. If we may also assume that the observed enthalpy difference at 715°K can be attributed entirely to vibrational effects, we calculate an average vibrational frequency of hydrogen in tantalum of 1350 cm⁻¹, with an estimated uncertainty of ± 50 cm⁻¹. Details of this calculation may be found in a recent paper by Dantzer *et al.* (11).

Note that this frequency is significantly larger than the value, 970 cm⁻¹, adopted in our earlier work, which was taken from the neutron-scattering study by Rush and Flotow (4) of hydrogen in vanadium. However, Rush and Flotow also found evidence for another hydrogen frequency of about 1400 cm⁻¹, particularly at high hydrogen concentrations.

Last year a new investigation of the localized vibrational modes of hydrogen in tantalum has been published by Yamada *et al.* (12). These authors studied tantalum-hydrogen alloys of composition TaH_{0.1}, TaH_{0.5}, and TaH_{0.7} by inelastic neutron scattering at 20 and 85°C. At the lower temperature the hydrogen atoms in TaH_{0.5} and TaH_{0.7} are ordered; at the higher temperature all alloys are disordered (12).

Yamada *et al.* confirmed the presence of two hydrogen frequencies at about 970 and 1410 cm⁻¹. However, in all cases they found that the integrated intensity of the high energy peak was greater than that of the low energy peak, and also that the relative intensity of the high energy peak increased very considerably on going from 20 to 85°C. If we are justified in extrapolating these observations to the very much higher temperature of our calorimetric measurements, we believe our calculated average frequency of 1350 ± 50 cm⁻¹ must be considered to be in very reasonable agreement with Yamada *et al.*

We are now ready to compare our experimental excess entropies with estimates based on contributions from vibrational, electronic, and degeneracy terms. We define the partial excess entropy of hydrogen through the relation

$$\bar{S}_{\text{H}}^{\text{E}} = \Delta\bar{S}_{\text{H}} + \frac{1}{2}S_{\text{H}_2}^{\circ} + R \ln [N_{\text{H}}/(1 - N_{\text{H}})]. \quad (1)$$

In this expression $\frac{1}{2}S_{\text{H}_2}^{\circ}$ represents the standard entropy of hydrogen gas at the considered temperature, while $-R \ln [N_{\text{H}}/(1 - N_{\text{H}})]$ represents the "ideal" (i.e., configurational) partial molar entropy, calculated under the assumption that the hydrogen atoms have access to only one interstitial lattice site per tantalum atom.

Our experimental values of $\bar{S}_{\text{H}}^{\text{E}}$ and $\bar{S}_{\text{D}}^{\text{E}}$ are plotted against composition in Fig. 2. We see that our extrapolated experimental value of $\bar{S}_{\text{H}}^{\text{E}}$ ($N_{\text{H}} = 0$) is 5.4 cal °K⁻¹ mole⁻¹; the corresponding value of $\bar{S}_{\text{D}}^{\text{E}}$ ($N_{\text{D}} = 0$) is 6.8 cal °K⁻¹ mole⁻¹. If we set $\tilde{\nu}_{\text{H}} = 1350$ cm⁻¹ and $\tilde{\nu}_{\text{D}} = 1350/\sqrt{2}^{1/2} = 955$ cm⁻¹, we calculate at 715°K, $\bar{S}_{\text{H}}^{\text{E}}(\text{vibr}) = 1.5$ cal °K⁻¹ mole⁻¹, and $\bar{S}_{\text{D}}^{\text{E}}(\text{vibr}) = 2.9$ cal °K⁻¹ mole⁻¹. The difference between these two values is in excellent agreement with the experimental difference.

Previously we estimated the electronic contribution to the partial excess entropy of hydrogen in tantalum near 700°K to be -0.7 ± 0.3 cal °K⁻¹ mole⁻¹. When this estimate is combined with the vibrational terms above and the sums subtracted from $\bar{S}_{\text{H}}^{\text{E}}$ and $\bar{S}_{\text{D}}^{\text{E}}$ we arrive at a value of 4.6 cal °K⁻¹ mole⁻¹ which must be accounted for by other entropy contributions. We believe a major part of this "residual" entropy must be attributed to the lattice degeneracy of hydrogen on the interstitial sites in the bcc structure.

It is well known that the bcc tantalum structure has six interstitial lattice sites per atom which are *tetrahedrally* surrounded by tantalum atoms (T sites), and three interstitial sites which are *octahedrally* coordinated (O sites).

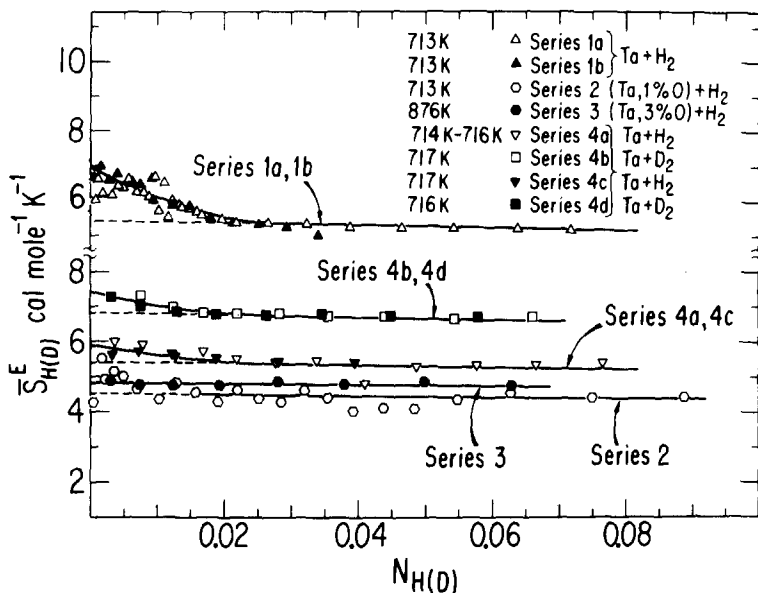


FIG. 2. Partial excess entropies of hydrogen and of deuterium at indicated temperatures plotted against mole fraction of H(D).

Most of the information presently available on hydrogen site occupancy in body-centered cubic metals is based on neutron-scattering investigations such as the already quoted study by Rush and Flotow (4). Confirming information has been provided by channeling experiments (13). Most of these studies have been carried out at or near room temperature, and seem to indicate that the hydrogen atoms prefer the T-sites. If this is indeed the case, the site degeneracy contribution to the partial entropy of hydrogen at $N_H = 0$ should be $R \ln 6 = 3.56 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$.

To the best of our knowledge no neutron-scattering study or channeling experiments on Ta + H₂ or Ta + D₂ have been carried out at temperatures approaching those of the present investigation. However, if the energy advantage of the T-sites compared to the O-sites is not large compared to RT , one might expect the hydrogen atoms to be distributed nearly randomly over both types of sites. In this event a lattice degeneracy term approaching $R \ln 9 = 4.37 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$ might be expected.

It will be apparent that both of these values ($R \ln 6$ and $R \ln 9$), in principle, would be consistent with the observed "residual" excess entropy of $4.6 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$. However, the value $R \ln 9$ would be acceptable only if other excess entropy terms are very small. There are at least two additional contributions which may be significant.

On the one hand, there presumably will be an entropy term associated with the modification of the vibrational spectrum of tantalum. In our previous study of the solutions of hydrogen in V, Nb, and Ta² we estimated this term from the Wagner volume expansion expression (14), $\bar{S}_H(\text{vol}) = (\alpha/\beta)\bar{V}_H$, where α is the coefficient of thermal expansion, β the isothermal compressibility, and \bar{V}_H the partial molar volume of hydrogen. For hydrogen in the considered metals this term represents about $+1.5 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$. However, this estimate does not take into account other terms which arise from the local compression and shear [Huntington *et al.* (15); Boureau *et al.* (16)]. The net effect of these other terms

probably is negative and may well be of comparable magnitude to the volume expansion term.

Finally, we want to mention again the high mobility of the hydrogen atoms. We previously suggested that this may possibly give rise to a "communal" entropy which at high temperature may approach R (2).

If we, in the light of this, consider the observed "residual" partial entropy of hydrogen in tantalum, we are led to conclude that there is strong evidence for a lattice degeneracy term of $R \ln 6$, consistent with hydrogen occupancy of the T-sites. On balance, it seems less likely that the hydrogen atoms should also occupy the O-sites at 715°K. However, our entropy data suggests that this possibility cannot be ruled out entirely.

Influence of Oxygen Impurities

An important feature of the present investigation is the new information it provides on the influence of interstitial oxygen on the equilibrium partial pressure of hydrogen, and also on the enthalpy of solution of hydrogen in tantalum. We refer here first to Fig. 3 which presents a plot of $\sqrt{P^{1/2}}$ against N_H for our Series 1a, 1b (Ta + H₂, 713°K), 4b (Ta + D₂, 717°K), 2 (Ta, 1 at.% O + H₂, 713°K), and 3 (Ta, 3 at.% O + H₂, 876°K).

Let us first compare the results of Series 1a, 1b, and 2. In this case we find an *increase* in the hydrogen equilibrium pressure of nearly 50% on going from pure tantalum to the oxygen containing solid solution. Thus the *solubility* of hydrogen (at a constant gas pressure) is reduced significantly by the presence of small amounts of oxygen in solid solution. However, our observed equilibrium pressures for tantalum with 3 at.% oxygen at 876°K are only about 10% higher than values for pure tantalum which can be interpolated from the data of Veleckis and Edwards (7) at 823 and 903°K. Thus, it is apparent that this situation is reversed at higher oxygen contents.

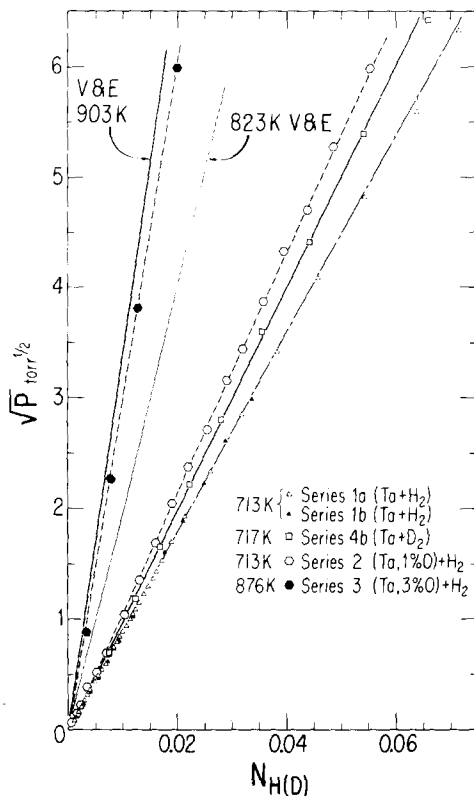


FIG. 3. Plots of $\sqrt{P^{1/2}}$ against mole fraction of hydrogen (deuterium) at indicated temperatures.

Let us turn next to Fig. 4, which shows a plot of the limiting values of $\Delta\bar{H}_H$ (at $N_H = 0$) against oxygen content. Note here that we find a near linear dependence of $\Delta\bar{H}_H$ on oxygen concentration; $\Delta\bar{H}_H$ becomes more negative as the oxygen content is increased. The slope of the straight line drawn in Fig. 4 is about -32

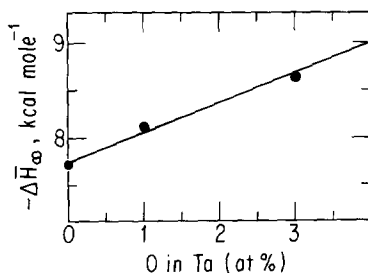


FIG. 4. Plot of the limiting values of the partial enthalpies of solution of hydrogen in tantalum ($\Delta\bar{H}^\infty$) against oxygen content.

kcal mole⁻¹ O. The magnitude of the negative slope clearly is a measure of the (apparent) attractive interaction between hydrogen and oxygen under the conditions of our experiments (see below). While this interaction in principle might be expected to give rise to some deviation from complete randomness in the relative distribution of hydrogen and oxygen atoms, the linear dependence of $\Delta\bar{H}_H$ on oxygen content indicates that nonrandomness should not be very significant at the considered low oxygen concentrations.

Without considering in detail the nature of the interstitial sites occupied by each solute atom, let us for simplicity assume that each hydrogen site is surrounded by 12 potential oxygen sites. Then we may formally attribute the slope in Fig. 4 to the creation of 12 hydrogen-oxygen pairs. This provides a crude estimate of the O-H pair energy of about 2.7 kcal/mole. We are not aware of any other thermodynamic data for tantalum that allow a check on this value. However, internal friction studies by Chang and Wert (18) on the interaction between oxygen and hydrogen in vanadium indicate an O-H pair energy of comparable magnitude (≈ 2.0 kcal), as does the work of Baker and Birnbaum (19) on the interaction between oxygen and hydrogen in niobium.

Let us consider further the data plotted in Fig. 4. In the analysis presented by Wagner (14) it was shown that one of the principal physical effects which might give rise to the negative slope in this figure is the lattice expansion which is associated with insertion of the oxygen atoms into the tantalum structure. At low solute concentration this lattice expansion term should, following Wagner [Eqs. (23)–(25)], be approximately $\bar{V}_H \bar{V}_O / V_{Ta} K_{Ta}$. Here V_{Ta} and K_{Ta} represent the molar volume (10.9 cm³) and compressibility (0.51×10^{-12} cm² dyn⁻¹) of tantalum; \bar{V}_H (1.6 cm³/mole) and \bar{V}_O (5.5 cm³/mole (20)) are the partial molar volumes of hydrogen and oxygen in tantalum, respectively. On this basis we calculate the (Wagner) volume contribution to

the slope in Fig. 4 to be about -38 kcal/mole. There are, of course, a number of other physical effects which may also be of importance, such as, e.g., the local compression and shear considered by Huntington (15), the modification of the electron to atom ratio, the mutual attraction or repulsion of solute atoms, etc. Even so, we note with interest that the difference between the calculated volume contribution and the experimentally observed slope of -32 kcal/mole is not very large.

A comparison of the equilibrium data in Fig. 3 and the enthalpy values in Fig. 4 also allows us to evaluate the influence of the oxygen impurities on the partial entropy of hydrogen in tantalum. For each hydrogen solid solution we may write

$$\Delta\bar{G}_H = RT \ln \sqrt{P^{1/2}} = \Delta\bar{H}_H - T\Delta\bar{S}_H. \quad (2)$$

In this expression $\Delta\bar{G}_H$, $\Delta\bar{H}_H$, and $\Delta\bar{S}_H$ represent the relative partial molar Gibbs energy, enthalpy, and entropy of hydrogen, respectively, all referred to the standard state of pure hydrogen gas at 1 atm of pressure. Let us designate all thermodynamic quantities which apply for the true binary tantalum-hydrogen system by the symbol*, i.e.,

$$\Delta\bar{G}_H^* = RT \ln (P^{1/2})^* = \Delta\bar{H}_H^* - T\Delta\bar{S}_H^*. \quad (3)$$

Hence we may write

$$\Delta\bar{G}_H - \Delta\bar{G}_H^* = RT \ln (P/P^*)^{1/2} = (\Delta\bar{H}_H - \Delta\bar{H}_H^*) - T(\Delta\bar{S}_H - \Delta\bar{S}_H^*). \quad (4)$$

From the data plotted in Figs. 3 and 4 we accordingly calculate for the alloy with 1 at.% O at 713°K:

$$\Delta\bar{S}_H - \Delta\bar{S}_H^* \approx -0.9 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1},$$

and for the alloy with 3 at.% O at 876°K:

$$\Delta\bar{S}_H - \Delta\bar{S}_H^* \approx -1.1 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}.$$

In the latter calculation we have set $P \approx 1.1P^*$ and have disregarded any possible dependence of $\Delta\bar{H}_H - \Delta\bar{H}_H^*$ on temperature. Our earlier work (1, 2) suggests that this will not introduce any significant error in the cal-

ulation. Note that the two calculated values of $\Delta\bar{S}_{\text{H}} - \Delta\bar{S}_{\text{H}}^*$ are of comparable magnitude; both indicate that at the considered temperatures the partial molar entropy of hydrogen is reduced by about $1 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$ through the presence of interstitial oxygen contents of the order of 1 to 3 at. %.

It is now possible to understand more fully the dependence of hydrogen solubility on oxygen content which we commented on above. For small oxygen contents in tantalum there is a small negative change in the partial enthalpy of solution of hydrogen, which is not large compared to the corresponding negative change in entropy. The net result will be a significant relative increase in the partial pressure of hydrogen. On the other hand, for larger oxygen contents ($N_{\text{O}} \gtrsim 0.03$), there will be a larger change in the partial enthalpy while the corresponding entropy change remains nearly constant. Hence, the equilibrium partial pressure of hydrogen eventually will fall below that of pure tantalum, i.e., the hydrogen solubility will be *increased* at constant pressure.

It remains to make a final brief remark about the reduction in the partial molar entropy of hydrogen caused by the oxygen impurities. It is possible to visualize that this entropy reduction may be caused by a number of factors such as, e.g., the modification of the vibrational spectrum of tantalum and/or of hydrogen, the preference of the hydrogen atoms for occupancy of sites near the oxygen atoms, a reduction in the communal entropy, etc. At the present time we are not ready to pursue this question beyond this purely speculative stage.

The Dilute Solution Anomaly

In our discussion of the dilute solution anomaly we again refer to Figs. 1 and 2, which give all the relevant enthalpy and entropy data. Note first that while there is reasonable internal agreement between the experimental enthalpy and entropy data for different runs at higher hydrogen contents, and also for the

values obtained by extrapolation of these results to $N_{\text{H}} = 0$, there is considerable difference between the extrapolated values and the experimental data in the dilute solution range. This difference represents about 10% for Series 1a, 1b, but only 2–3% for Series 4a, 4c. In each case the observed values in the dilute range are more endothermic than the extrapolated ones. It is apparent that the extent of the dilute solution anomaly reflects the "pretreatment" of the tantalum metal, i.e., the past history of the sample. Since the metal foil pretreated at the higher temperature (850°C) shows only a small anomaly, we infer that the anomaly probably is related to the extent and type of lattice imperfection which remains in the sample after the pretreatment. However, further analysis of this problem clearly would require careful physical examination of the samples both before and after hydrogen absorption.

It is not indicated by our results that the oxygen content plays a major role in determining the extent of the dilute solution anomaly. Thus we see that our Series 2, with an oxygen content of 1 at. % O, and with the measurements carried out at 713°K , shows a dilute solution anomaly somewhat larger than for Series 4, but much smaller than for Series 1. However, the experimental scatter of the data in Series 2 is significantly larger than for the measurements with pure tantalum at the same temperature. This principally reflects the lower absorption rate for hydrogen in the alloy. When we attempted to extend the hydrogen absorption experiments at 713°K to an alloy with 3 at. % O, we found that the rate was much too slow for effective calorimetry. For this reason we carried out our experiments with this alloy at a higher temperature (876°K). For this high-temperature series the dilute solution anomaly in the partial enthalpy is no longer observed.

Acknowledgments

We acknowledge discussions with G. Boureau regarding the significance of the results.

This research was supported by the National Science Foundation (Grant DMR75-08175), and has also benefited from the support of materials science at The University of Chicago provided by the NSF-MRL.

Note added in proof. Since this paper went to press, Magerl *et al.* (*J. Phys. Chem. Solids* **38**, 683 (1977)) also have considered the excess entropy of hydrogen in tantalum. The authors, from their own unpublished neutron scattering data, have estimated the partial entropy term associated with the modification of the vibrational spectrum of tantalum to be *negative* (rather than near zero, as assumed above). If we adopt their value, $\sim 1.5 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$, the modified "residual" entropy of our own discussion above will be $6.1 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$ near 700°K . This leaves ample room both for lattice degeneracy (even for a term as large as $R \ln 9 = 4.37 \text{ cal } ^\circ\text{K}^{-1} \text{ mole}^{-1}$, consistent with hydrogen occupancy of *both* T and O sites) and for a "communal" entropy term of the order of R .

References

- O. J. KLEPPA, M. E. MELNICHAK, AND T. V. CHARLU, *J. Chem. Thermodyn.* **5**, 595 (1973).
- O. J. KLEPPA, P. DANTZER, AND M. E. MELNICHAK, *J. Chem. Phys.* **61**, 4048 (1974).
- M. O'KEEFFE AND S. A. STEWART, *Ber. Bunsenges. Phys. Chem.* **76**, 1278 (1972).
- J. J. RUSH AND H. E. FLOTOW, *J. Chem. Phys.* **48**, 3795 (1968).
- P. KOFSTAD, W. E. WALLACE, AND L. J. HYVÖNEN, *J. Amer. Chem. Soc.* **81**, 5015 (1959).
- O. M. KATZ AND E. A. GULBRANSEN, in "Columbium Metallurgy" (D. L. Douglass and F. W. Kunz, Eds.), Interscience, New York (1962).
- E. VELECKIS AND R. K. EDWARDS, *J. Phys. Chem.* **73**, 683 (1969).
- A. D. MCQUILLAN AND A. D. WALLBANK, *J. Chem. Phys.* **51**, 1026 (1969); **52**, 965 (1970).
- A. D. WALLBANK AND A. D. MCQUILLAN, *J. Chem. Soc., Faraday Trans. 1* **71**, 685 (1975).
- G. BOUREAU AND O. J. KLEPPA, *J. Chem. Thermodyn.*, in press.
- P. DANTZER, O. J. KLEPPA, AND M. E. MELNICHAK, *J. Chem. Phys.* **64**, 139 (1976).
- R. YAMADA, N. WATANABE, K. SATO, H. ASANO, AND M. HIRABAYASHI, *J. Phys. Soc. Japan* **41**, 85 (1976).
- See, e.g., M. ANTONINI AND H. D. CARSTANJEN, *Phys. Status Solidi (a)* **34**, K153 (1976).
- C. WAGNER, *Acta Metall.* **19**, 843 (1971).
- H. B. HUNTINGTON, G. A. SHIRN, AND E. S. WAJDA, *Phys. Rev.* **99**, 1085 (1955).
- G. BOUREAU, O. J. KLEPPA, AND P. DANTZER, *J. Chem. Phys.* **64**, 5247 (1976).
- P. P. MATYASH, N. A. SKAKUN, AND N. P. DIKII, *JETP Lett.* **19**, 18 (1974).
- H. Y. CHANG AND C. A. WERT, *Acta Metall.* **21**, 1233 (1973).
- C. BAKER AND H. K. BIRNBAUM, *Acta Metall.* **21**, 865 (1973).
- D. A. VAUGHAN, O. J. STEWART, AND C. M. SCHWARTZ, *Trans. AIME* **221**, 937 (1961).