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Thermodynamics of Formation of Tantalum–Hydrogen Solid Solutions from Vapor Pressure Data[1]

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Vapor pressures of the tantalum–hydrogen system have been measured for temperatures ranging from 164 to 402° and for alloys containing from 0.1 to $33^1/_3$ atomic % hydrogen. The data for temperatures between 300 and 400° were treated to obtain partial molal free energies, entropies and enthalpies, and the free energies, entropies and heats of formation of the solid solutions. The data are in agreement with Sievert's Law only at intermediate concentrations. Positive deviations occur at high concentrations due to a progressive filling of interstitial sites and a reduction in the entropy of the system. Complex behavior is observed in dilute solutions, originating, it is thought, with gaseous impurities (oxygen and nitrogen) in the sample. The partial heat of vaporization is only about half as large in dilute solutions as in concentrated solutions and the entropy of dissolved hydrogen is unexpectedly high. The reason for this behavior is not clear.

In 1940 Kelley published[4] results of a study of the low temperature heat capacities of a series of Ta–H alloys. His data revealed the existence of λ-points for these alloys in the temperature interval extending from about 100 to 300°K., the λ-point temperature being observed to increase with increasing hydrogen content of the sample. X-Ray diffraction studies carried out in this Laboratory several years ago indicated[5] that for the compositions used in Kelley's work the Ta–H system at his lowest temperatures consists of two phases and furthermore that the thermal anomalies which he observed probably were due to the conversion of the two phase system into a single phase solid solution as temperature is increased. The diffraction study showed that at very low temperatures the hydrogen contained in the system is almost entirely in a body centered tetragonal phase whose formula is approximately Ta_2H. With increasing temperature the tetragonal phase is progressively destroyed. Hydrogen is transferred from this phase to the other phase, which consists of elemental tantalum containing a minute amount of dissolved hydrogen, until the hydrogen concentration becomes uniform throughout the specimen. The transfer process is endothermal and gives rise to the rather broad λ-points observed by Kelley.

Recent heat capacity studies of the hydride Ta_2H carried out[6] in this Laboratory show a very sharp λ-point at 315°K. This thermal anomaly differs from those observed by Kelley not only in its sharpness but also in that it was thought to be due to a rearrangement of the protons in the manyfold more abundant interstitial sites in the sample. This hypothesis was confirmed by subjecting a sample of Ta_2D to neutron diffraction analysis. A rearrangement of the protons at the λ-point is clearly indicated. At high temperatures the protons are found to be randomly distributed in the tetrahedral interstices. Observations show that they exist in a more orderly arrangement below the λ-point. However, at these temperatures the neutron diffraction patterns are complex to the point that they have not as yet been successfully interpreted so as to indicate the positions of the deuterons. One complication in attempts to solve this structure is that it is not clear whether or not Ta_2D exists as a unique structure, that is, one for which the deuterons exist in a single configuration. This issue can be settled by ascertaining the residual entropy of the hydride.[7] It was with this

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[1] This work was assisted by the U. S. Atomic Energy Commission.

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[4] K. K. Kelley, *J. Chem. Phys.*, **8**, 316 (1940).

[5] T. R. Waite, W. E. Wallace and R. S. Craig, *ibid.*, **24**, 634 (1956).

[6] Unpublished measurements of W. G. Saba and W. E. Wallace.

[7] The neutron diffraction studies show that the structure is the same throughout the temperature range from 4 to 300°K.

specific objective in mind that the present measurements were undertaken. This work represents the first step in a series of studies which will lead to the evaluation of the residual entropy of Ta_2H. It has been found, however, that the measured thermodynamic properties of this system have a number of unusual features which make them of interest quite apart from the issue of the zero point entropy of the hydride, and seemingly appropriate for presentation at this time.

A few vapor pressure determinations for the Ta–H system have been made previously by Sieverts, *et al.*[8,9] These studies, which covered temperatures above 400° and involved but a few compositions, are of no value in determining thermodynamic data for the system. However, the fragmentary results obtained were found to be in substantial agreement with those of this study.

Experimental Details

Apparatus.—The essential parts of the apparatus were (1) a high temperature thermostat, (2) a McLeod gauge and an ordinary manometer, (3) a gas buret, (4) a Vycor sample tube and (5) a high vacuum pumping unit consisting of two mercury diffusion pumps connected in series.

The high temperature thermostat was merely a tube furnace whose temperature was controlled electronically. A platinum resistance thermometer was the temperature sensing element. It constituted one arm of a balanced bridge. A drift of temperature unbalanced the bridge and supplied a signal to a control circuit for a thyratron, which provided the current for the thermostat heater. The signal produced an adjustment in current and restored the temperature to its preset value. Control to ± 0.1° was achieved.

To ensure uniform temperature over the sample, the sample tube slid into a hole in a copper bar (1" diam.) which in turn was placed in the tube furnace. The temperature gradient along the sample did not exceed 0.2°. Two other holes in the copper bar accommodated the platinum resistance thermometer and an iron–constantan thermocouple. Blank determinations showed that the temperature inside the sample tube was the same as in the copper bar.

The McLeod gauge had in addition to the usual capillary, two bulbs so that its range extended from 10^{-6} to 12 mm. Above this range pressures were measured with the manometer, read by a cathetometer, thereby extending the pressure range up to atmospheric pressure.

The sample was held in a Vycor tube so that it could be baked out at 900° in high vacuum to degas it and to remove all dissolved hydrogen prior to initiating a series of determinations. The sample tube was attached to the rest of the assembly with a Vycor-to-Pyrex graded seal. A gold trap was incorporated in the system to protect the sample from possible contamination by mercury vapor.

Materials Employed.—The tantalum was in the form of 3 mil foil. It was obtained from the Fansteel Metallurgical Co. and was stated to be 99.9% pure or better. The material employed was examined spectroscopically and only Nb, Fe, Ca, Cr, Mo and V were detected. Estimates of the maximum amounts of impurity present were these: Nb and Fe—each 0.01%, the others—each 0.001%. The tantalum was known to contain a few hundredths of a per cent. of oxygen and nitrogen, and, as will be indicated in the Discussion section, some unsuccessful attempts were made to perform measurements using specimens from which these gaseous impurities had been removed.

The hydrogen was commercial tank gas which was purified by passing through a Deoxo unit and then a liquid nitrogen trap. It was further purified by passage through a palladium barrier.

Procedure.—The sample was prepared by polishing the foil with emery cloth under oil and subsequently degreasing and cleaning it in toluene, acetone and ether. A weighed amount of the sample was placed in the Vycor tube, which then was sealed onto the remainder of the system and evacuated to 10^{-6} mm. or better. The sample was baked out as indicated above and the entire system was degassed by torching. When the system was found to be adequately degassed and also completely tight, a measured quantity of hydrogen was introduced using the buret system. The composition of the alloy was computed from the amount of hydrogen introduced, after corrections were made for hydrogen retained in the dead space.

The hydrogen was adsorbed in the metal at temperatures ranging from 160 to 405°, after which measurements were made at 10 temperatures—164, 193, 223, 250, 278, 304, 324, 349.5, 376 and 402°. Temperature was cycled between the extremes and the equilibrium vapor pressures were thus determined by approaching from both high and low temperatures. It was the usual practice to raise the temperature to 900° at the conclusion of a series of determinations at a particular composition[10] and remove the hydrogen completely prior to re-hydrogenating for the next series. In a few instances withdrawal was stopped short of completion, the amount of hydrogen withdrawn was determined and measurements on the sample were made and compared with those obtained using a sample prepared by hydrogenating freshly baked out tantalum to the same composition. This comparison showed the results to be independent of the direction of approach to the composition under examination. The temperature cycling indicated results which were free of hysteresis except at low concentrations at low temperatures. The ranges in which it was doubtful that true equilibrium was attained will be indicated in the next section.

Results

Experimental Data.—According to the equation for the dissolution of hydrogen in metals, $H_2(\text{gas}) \rightarrow 2H(\text{metal})$, one would expect P to vary linearly with N_H^2 if the solid solution is ideal. P and N_H are the vapor pressure of H_2 and atomic fraction of hydrogen in solid solution, respectively. This linearity of P_{H_2} with N_H^2 is the well-known Sievert's Law. From this one expects $\sqrt{P}/N_H$ to be constant at constant temperature so long as the solid solution is behaving ideally. Since the temperature range involved in the present measurements lies well above the temperature at which hydride formation occurs, agreement with Sievert's Law was expected, at least at low hydrogen concentrations. To facilitate comparison of the observed results with the behavior expected the data are listed in Table I, as $\log \sqrt{P}/N_H$ for various compositions. Since the raw data are exceedingly voluminous, only values at rounded compositions are given. The experimental results are shown in graphical form in Fig. 1. The region in which equilibrium may not have been attained lies to the lower left of the dashed lines.

Calculation of Thermodynamic Properties.—If a proper extrapolation to zero concentration can be made, the free energies, entropies and heats of formation of the solid solutions can be computed from the observed vapor pressures. The relative partial molal free energy, $\bar{F}_H - {}^1/_2F^\circ_{H_2}$, for hydrogen is obtained from $RT/2 \ln P$, where P is the observed vapor pressure. The free energies of formation ΔF_f per gram atom of alloy were calculated from the measured vapor pressures using the expression

$$\Delta F_f = RT\left[N_H \ln N_H + (1 - N_H)\ln(1 - N_H) + (1 - N_H)\int_0^{N_H} \ln \frac{\sqrt{P}}{N_H}\, d\left(\frac{N_H}{1 - N_H}\right)\right]$$

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[8] A. Sieverts and E. Bergner, *Ber.*, **44**, 2394 (1911).

[9] A. Sieverts and H. Brüning, *Z. physik. Chem.*, **A174**, 365 (1935).

[10] Actually the composition varied slightly with the temperature since the amount of hydrogen in the gaseous phase contained in the dead space increases with pressure.

TABLE I

VAPOR PRESSURE ISOTHERMS FOR Ta–H SOLID SOLUTIONS[a]

	$\text{Log}\,\frac{\sqrt{P}}{N_H}$									
100 N_H	164°	193°	223°	250°	278°	304°	324°	349.5°	376°	402°
0.10				1.140	1.230	1.327	1.403			
.25				1.150	1.234	1.345	1.430	1.545	1.645	1.750
.50			1.070	1.155	1.255	1.378	1.470	1.594	1.690	1.791
1.00		0.694	0.842	0.992	1.148	1.296	1.401	1.550	1.683	1.800
2.00		.601	.786	.958	1.140	1.295	1.410	1.565	1.694	1.819
5.00	0.300	.519	.744	.947	1.139	1.305	1.420	1.579	1.700	1.819
10.0	.200	.471	.727	.937	1.132	1.305	1.420	1.579	1.700	1.819
15.0	.171	.453	.718	.931	1.130	1.305	1.420	1.579	1.698	1.819
20.0	.173	.460	.721	.936	1.136	1.307	1.423	1.581	1.706	1.822
25.0	.216	.507	.770	.981	1.183	1.351	1.470	1.637	1.760	1.882
30.0		.652	.911	1.122	1.314	1.487	1.613	1.757	1.888	(2.011)[b]
33.3		.848	1.096	1.300	1.487	1.649	1.777	(1.909)	(2.039)	(2.158)

[a] P is the pressure of hydrogen in mm. and N_H is the atomic fraction of H. Temperature is in °C. [b] Values in parentheses are extrapolated values from the lower temperature isotherms.

This relationship is obtained when one substitutes for the relative partial molal free energies in the expression

$$\Delta F_f = N_H\left(\bar{F}_H - \frac{1}{2}F^0_{H_2}\right) + (1 - N_H)(\bar{F}_{Ta} - F^0_{Ta})$$

As indicated above the value for hydrogen is $RT/2$ ln P. The corresponding quantity for tantalum is obtained by integration of the Gibbs–Duhem equation. The resulting equation then was integrated by parts to yield the expression cited above. The five lowest isotherms were not included in the treatment since there were serious doubts as to how the extrapolation should be made in these cases. The extrapolation for the five isotherms used was made by simple extension of the horizontal portions of the curves observed for N_H less than about 0.18. This ignores the departure from linearity below 0.04. The justification for following this procedure will be presented later. At this point it should be remarked that integration using the observed data below $N_H = 0.04$ would lead to results which are practically identical with those listed in Table I provided that the $\sqrt{P}/N_H$ values in the region of extrapolation agree with those observed experimentally within the rather wide latitude of about two orders of magnitude.

Plots of ΔF_f and $\bar{F}_H - {}^1/_2\,F^0_{H_2}$ *versus* temperature are linear showing ΔS_f and $\bar{S}_H - {}^1/_2S^0_{H_2}$ to be constant within the limit of experimental error over the range of temperature studied. These entropies were evaluated from the slopes of the plots and were combined with the corresponding free energies to give ΔH_f and $\bar{H}_H - {}^1/_2H^0_{H_2}$. These quantities were also invariant with temperature. Average values for the temperature range 300 to 400° for ΔS_f, ΔH_f and the relative partial molal entropies and enthalpies of hydrogen are given in Table II together with corresponding free energy values for 350°. The scatter in the vapor pressures was of the order of 1%. This introduces uncertainties of about 1%, 3 to 5% and 2% into ΔF_f, ΔS_f and ΔH_f, respectively. The estimated error in $\bar{F}_H - {}^1/_2F^0_{H_2}$ ranges from 10 cal. at $N_H = 0.05$ to about 2 cal. for $N_H = 0.333$. The partial molal entropies and enthalpies are uncertain by roughly 2 and 1%, respectively.

Discussion of Results

The data plotted in Fig. 1 show significant deviations from Sievert's Law at both extremes of concentration. The origin of the deviations at high concentrations is fairly clear. They are not due to factors which make hydrogen retention by the lattice energetically unfavorable since the data in Table II show that the partial heat of vaporization increases when the hydrogen content of the system increases from 20 to 30 atomic per cent. The high concentration deviations are

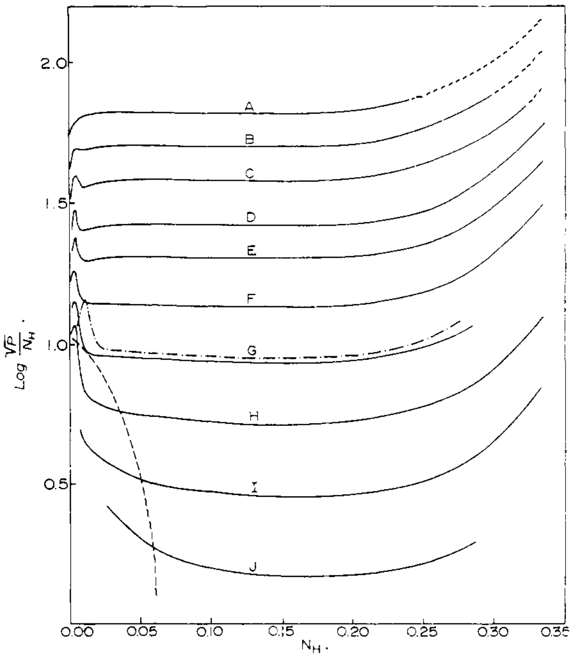

Fig. 1.—Vapor pressure data for tantalum–hydrogen system. Plot shows log $\sqrt{P}/N_H$ *versus* N_H for various temperatures: A, 402°; B, 376°; C, 349.5°; D, 324°; E, 304°; F, 278°; G, 250°; H, 223°; I, 193°; J, 164°. P is the hydrogen pressure in mm.; N_H is the atomic fraction of H. Data for "as received" tantalum ———. Isotherm at 250° for tantalum contaminated with 0.56 atomic % oxygen — · —. Region in which equilibrium conditions may not have been reached lies to the lower left of dashed line.

TABLE II

THERMODYNAMIC DATA FOR Ta–H SOLID SOLUTIONS AT 350°

N_H	0.05	0.10	0.15	0.20	0.25	0.30	0.333
ΔF_f,[a] cal./g. atom	− 230	− 370	− 470	− 540	− 600	− 620	− 600
ΔS_f,[a] e.u./g. atom	− 0.40	− 0.92	− 1.5	− 2.1	− 2.8	− 3.6	− 4.08
ΔH_f,[a] cal./g. atom	− 480	− 940	−1410	−1860	−2370	−2860	−3180
$\bar{F}_H - \frac{F^0_{H_2}}{2}$, cal./g. atom	−3310	−2510	−2010	−1600	−1210	− 520	− 1
$\bar{S}_H - \frac{S^0_{H_2}}{2}$, e.u./g. atom	− 9.9	− 11.1	− 12.1	− 12.7	− 13.6	− 14.8	− 14.9
$\bar{H}_H - \frac{H^0_{H_2}}{2}$, cal./g. atom	−9500	−9400	−9500	−9500	−9700	−9700	−9300

[a] These data are for 1 g. atom of solid solution.

due to entropy effects. As the hydrogen content of the system is increased, the number of sites available to new additions of hydrogen is progressively reduced, leading to a rapidly falling partial molal entropy. This gives a higher partial molal free energy which in turn gives rise to a larger vapor pressure of hydrogen than would otherwise have been developed.

The origin of the deviations from Sievert's Law at low concentrations is somewhat more obscure. Before regarding them to be a property of the tantalum–hydrogen, it is necessary to consider the possibility that they result from (1) instrumental error or (2) impurities in the solvent metal. The former can be excluded by noting that plots of log P *versus* $1/T$ exhibit good linearity for these concentrations. Faulty calibration or leaks, the most likely sources of instrumental error, would lead to deviations from linearity in the log P *vs.* $1/T$ plots.

Experiments designed to ascertain whether or not the low concentration deviations were an impurity effect were not conclusive. However, they did seem to point to impurities as the source of the difficulty. Efforts were made to prepare samples of tantalum which were relatively free of interstitial oxygen and nitrogen. These impurities, particularly oxygen, can be readily detected by their characteristic internal friction peaks. The oxygen peak in the "as received" tantalum was quite prominent. It disappeared in samples which had been "flashed," that is, heated to about 2500° in high vacuum. Attempts were made to measure the vapor pressure using flashed tantalum but these were entirely unsuccessful. The samples were either passive to hydrogen or absorbed with great reluctance. In neither case could thermodynamic equilibrium be achieved.[11] It was possible, however, to obtain data with samples which were deliberately contaminated with oxygen to see whether the anomalous behavior at low concentrations could be exaggerated. Tantalum was heated in oxygen at 900° and the oxygen uptake followed gasometrically. Isotherms then were determined at 193, 223, 250, 278, 304 and 324° on a sample whose oxygen content had been increased by 0.56 atomic %. Data from the 250° isotherm, which is typical, are included in Fig. 1. If one disregards for the moment the very dilute solutions, one sees that the effect of an increase in oxygen content is to diminish slightly the hydrogen solubility. In this respect the results resemble the findings of Martin and Rees[12] for the zirconium–hydrogen–oxygen system. They observed a steadily diminishing hydrogen solubility in zirconium with increasing amounts of oxygen and attributed this effect to the blocking of sites by the dissolved oxygen. If oxygen acts similarly in tantalum, the results indicate that the introduction of each oxygen atom extinguishes the solvent power of roughly 11 to 12 metal atoms. Furthermore, if the interstices involved in solubility are the tetrahedral sites, each oxygen atom is blocking out 60 to 70 interstitial positions. Although this number is quite large when compared to that observed by Martin and Rees, it does not seem unreasonably large since this many interstitial sites occur within a distance of less than 2 atomic diameters from the impurity atom.

If one now considers the behavior in dilute solutions, it is seen that the large positive deviations from Sievert's Law set in at higher concentrations for the oxygenated material. This suggests that these deviations are due to impurities in the material, a viewpoint which is also supported by the data plotted in Fig. 2. The rapid drop in partial heat of vaporization at low hydrogen concentrations is striking and puzzling. In view of the effect of added oxygen it seems reasonable to suppose that the reduction in the heat of vaporization is due to effects which originate in some way with the impurities which are present in the lattice. It is this reduction in heat of vaporization which produces the rise in vapor pressure (above the expected value) in the dilute solutions. On this basis the positive deviations at low concentrations are regarded, at least for the present, as due to impurities. It was for this reason that the linear horizontal portion was extrapolated to zero concentration in computing the thermodynamic properties of the system.

There is one additional feature of the dilute solutions which merits comment. The positive deviations pass through a maximum with increasing dilution. This maximum becomes less pronounced at higher temperatures and finally disappears entirely in the 402° isotherm. It is the vapor pressure behavior on the high dilution side of the

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(11) It is not clear why this behavior is exhibited. It may be that the impurities produce disturbances in the lattice which facilitate the entry of hydrogen, or it may be that the grain size is increased during the flashing, resulting in a slower hydrogenation process.

(12) S. L. H. Martin and A. L. G. Rees, *Trans. Faraday Soc.*, **50**, 343 (1954).

peak that is of interest. The rapid fall with increased dilution does not result from energy factors. In this composition region the partial heat of vaporization is diminishing rapidly as N_H is reduced. The negative deviations at the highest dilutions imply an abnormally high partial molal entropy for the hydrogen. Thus both the entropy and enthalpy of hydrogen in the very dilute solutions are higher than would have been inferred from the properties of the more concentrated system. Furthermore, increase of the oxygen content of the sample accentuates not only the rise in the enthalpy but that of the entropy as well. It is to be noted that at the highest temperatures there are no positive deviations from Sievert's Law at high dilutions. This behavior is a result of the anomalously high entropy in these solutions. The excess entropy becomes relatively more important at higher temperatures and finally overbalances the effect of the reduced heat of vaporization, as is observed in the two highest isotherms.

The source of the extra entropy and enthalpy in the dilute solutions is not at all clear. Nor is there a clear understanding of the way in which the impurities exert their influence. Perhaps the proton is screened by an electron in a bound orbital and dilution results in ionization. Another notion, which is equally speculative, is that in the concentrated solutions the system of protons is "solid-like" whereas in the most dilute solutions they are essentially "gas-like." According to this idea the hydrogen in the concentrated solution is localized and sits in an interstitial site. In the dilute solution the unit cell is smaller and the interstitial site correspondingly reduced in size. Under these circumstances coulombic repulsion of the proton might raise its energy to the point that it escapes from the interstitial site and travels through the lattice as if it were a gas. The surplus enthalpy and entropy of the hydrogen in the dilute solution would result from its "sublimation" into the lattice.

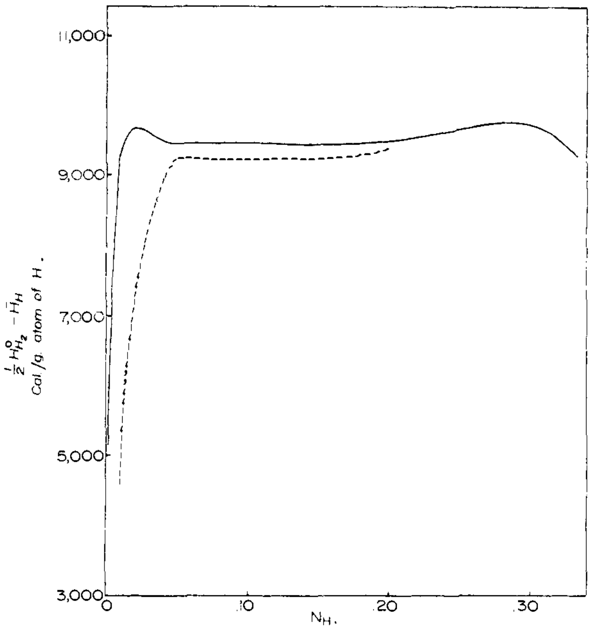

Fig. 2.—Plot of the partial heat of vaporization of hydrogen ($^1/_2 H^0_{H_2} - \bar{H}_H$) *versus* the atomic fraction of hydrogen (N_H) dissolved in tantalum. Data for "as received" tantalum ———; for tantalum which was contaminated with 0.56 atomic % oxygen – – – –.

Evaluation of these and other ideas which may be advanced clearly calls for additional and more intensive studies of the dilute solutions, preferably ones which are free of gaseous impurities. To accomplish this it will first be necessary to devise means to study them experimentally.

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION NO. 1040 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

Vapor Pressure Studies of the Vanadium–Hydrogen System and Thermodynamics of Formation of Vanadium–Hydrogen Solid Solutions[1]

BY PER KOFSTAD[2] AND W. E. WALLACE

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Vapor pressure data for the vanadium–hydrogen system have been obtained for temperatures extending from 165 to 456° and for compositions from 0.5 to 33 atomic % hydrogen. The data have been used to evaluate the thermodynamic properties of the system. Since no invariancy of vapor pressure with composition occurs, the results pertain to a single phase, the primary solid solution based on vanadium. Appreciable deviations from Sieverts' Law are observed. The results seem to imply the existence of two types of sites which are being occupied by hydrogen, the regular interstitial sites in the normal lattice and atypical sites, which occur at disturbed regions in the lattice.

In a study of the equilibrium vapor pressures of the Ta–H system as functions of temperature and composition,[3] unexpected deviations from Sieverts' Law were observed at small concentrations of hydrogen (<2 atomic %). As similar deviations have not been reported previously in the literature, it was of interest to see if other Vb metals exhibited like behavior. It was with this objective in mind that the present study was undertaken. However, the vanadium–hydrogen system is of additional interest in that published data concerning it are rather meager. There is a lack of information concerning the vapor pressure of hydrogen dissolved in pure vanadium and furthermore the constitution of the system is yet to be elucidated.

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(1) This work was assisted by the U. S. Atomic Energy Commission.

(2) On leave from the Central Institute for Industrial Research, Blindern, Oslo, Norway.

(3) P. Kofstad, W. E. Wallace and L. J. Hyvönen, THIS JOURNAL, **81**, 5015 (1959).