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.

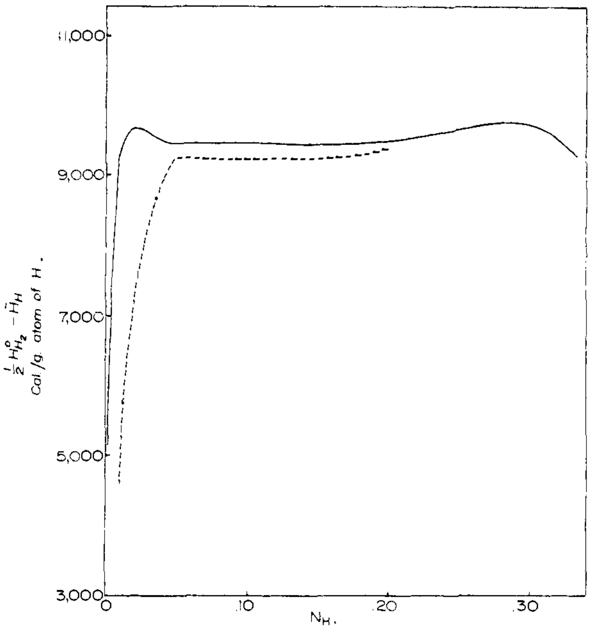

Fig. 2.—Plot of the partial heat of vaporization of hydrogen ($^1/_2 H^0_{H_2} - \bar{H}_H$) *versus* the atomic fraction of hydrogen (N_H) dissolved in tantalum. Data for "as received" tantalum ———; for tantalum which was contaminated with 0.56 atomic % oxygen - - - -.

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

RECEIVED MARCH 10, 1959

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.

[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).

Early investigations of the vapor pressure of the vanadium–hydrogen system were made by Sieverts, *et al.*[4] However, the results which were obtained were for rather impure vanadium. Its purity was 93.2%, the main contaminant being considered to be oxygen. They measured isotherms and isobars up to 1100° and observed the following: (1) absorption of hydrogen by vanadium was exothermic and was accompanied by a decrease in density, (2) below 300° absorption was slow and equilibrium could not be established and (3) the solubility increased with increasing purity of the metal, this effect, however, decreasing with increasing temperature. As will be shown later, the solubilities found in the present investigation are significantly higher than those reported by Sieverts, *et al.*

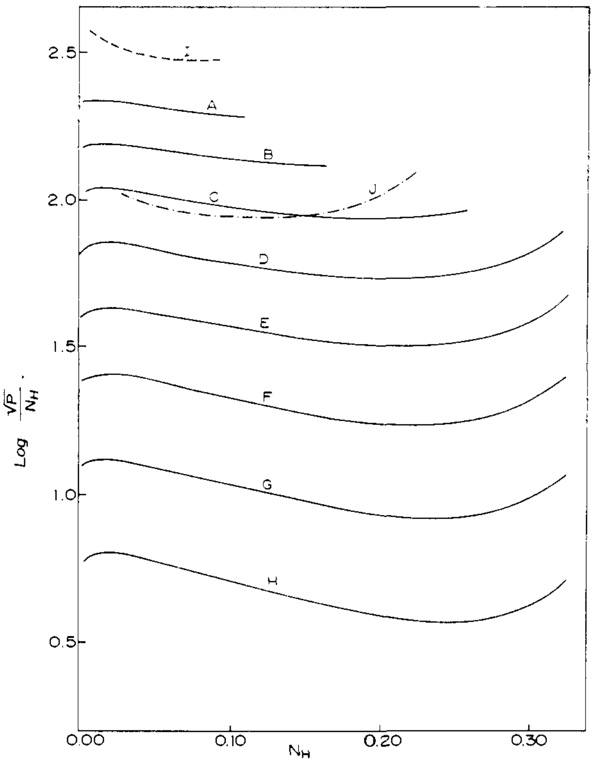

Fig. 1.—Vapor pressure data for the vanadium–hydrogen system. Plot shows log $\sqrt{P}/N_H$ for various temperatures: A, 456°; B, 413°; C, 371.6°; D, 329.5°; E, 287.5°; F, 245.8°; G, 204.3°; H, 164.5°. P is the hydrogen pressure in mm.; N_H is the atomic fraction of hydrogen. Dashed lines show data obtained by Sieverts, *et al.*[4]: I, 400°; J, 300°.

Attempts were made by Hägg to establish the constitution diagram for the system using X-ray diffraction techniques.[5] He found no shift in the diffraction lines upon absorption of hydrogen. New lines were observed, however, suggesting the existence of another phase, but the lines were too weak and diffuse to permit the diffraction pattern to be interpreted.

Experimental

The apparatus used and procedure followed were the same as those employed in the study of the tantalum–hydrogen system. The vanadium was furnished by the Electro Metallurgical Company. According to the supplier its carbon, nitrogen and oxygen content were each less than 0.1%. The sample used in the present work was analyzed spectroscopically and Ba, Cr, Fe, Mg, Mn, Mo, Ni, Si and Ti were detected. Estimates of maximum amounts of these impurities were: Fe, Mg and Mn, each 0.01%; the others, each 0.001%. Thus the purity exceeded 99.7%. The sample was in the form of a sheet 0.25 mm. in thickness from which were cut strips 7 cm. × 0.5 cm.

Experimental Results

Since the raw data are exceedingly voluminous, only values at rounded compositions are presented. These are given as log $\sqrt{P}/N_H$ in Table I and are shown graphically in Fig. 1. (P is the vapor pressure of hydrogen in mm. and N_H is the atomic fraction of H.) For comparison isotherms obtained by Sieverts, *et al.*,[4] at 300° and 400° are also included in the plot. In no case was hysteresis observed in the present study. However, at the lowest temperatures as long as 24 hr. was needed for equilibration of samples with large hydrogen content.

TABLE I

VAPOR PRESSURE ISOTHERMS FOR THE VANADIUM–HYDROGEN SYSTEM[a]

Log $\sqrt{P}/N_H$

100 N_H	164.5°	204.3°	245.8°	287.5°	329.5°	371.6°	413.0°	456.0°
0.5	0.783	1.113	1.393	1.618	1.836	2.026	2.180	2.331
2.0	.809	1.120	1.401	1.632	1.857	2.032	2.186	2.332
4.0	.784	1.100	1.388	1.620	1.839	2.019	2.171	2.312
8.0	.733	1.054	1.347	1.586	1.808	1.984	2.147	2.290
12.0	.682	1.012	1.308	1.550	1.767	1.959	2.128	
16.0	.632	0.971	1.266	1.521	1.743	1.942		
20.0	.592	.932	1.239	1.502	1.730	1.935		
24.0	.566	.920	1.237	1.505	1.739	1.943		
28.0	.588	.949	1.278	1.543	1.779			
32.0	.691	1.054	1.383	1.652	1.882			

[a] P is the pressure of hydrogen in mm. of Hg and N_H is the atomic fraction of H. Temperature is in °C.

Since the vapor pressures obtained in the present study were in no instance independent of composition, the system consists of a single phase throughout the ranges of temperature and composition studied. Thus the results obtained are for the primary solid solutions based on vanadium. This finding represents no conflict with the work of Hägg,[5] which indicated a two phase system. His observations were for room temperature, and it may be that precipitation from the primary solid solution occurs on cooling, as is the case with the Ta–H system.[6]

The data were used to compute the partial molal quantities of the components in the system and these were then used to evaluate the changes in free energy, enthalpy and entropy which accompany the formation of the solid solution from the elements. Results of these calculations, which were made employing the same procedure as that used in the earlier study,[3] are shown in Table II.

Extrapolation to infinite dilution, which is needed to integrate the Gibbs–Duhem equation, was made by linearly extending the log $\sqrt{P}/N_H$ *versus* N_H curve below N_H = 0.005, the lowest

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(4) L. Kirschfeld and A. Sieverts, *Z. Elektrochem.*, **36**, 123 (1930). This paper contains references to earlier work on the system.

(5) G. Hägg, *Z. physik. Chem.*, **B11**, 433 (1931).

(6) T. R. Waite, W. E. Wallace and R. S. Craig, *J. Chem. Phys.*, **24**, 634 (1956).

TABLE II

THERMODYNAMIC DATA FOR THE VANADIUM–HYDROGEN SYSTEM AT 310°

N_H	0.05	0.10	0.15	0.20	0.25	0.30	0.333
$\Delta F_f{}^a$ (cal./g. atom)	− 189	− 300	− 382	− 448	− 495	− 520	− 517
$\Delta H_f{}^a$ (cal./g. atom)	− 387	− 772	− 1175	− 1585	− 2020	− 2470	− 2760
$\Delta S_f{}^a$ (e.u./g. atom)	− 0.34	− 0.81	− 1.36	− 1.95	− 2.62	− 3.34	− 3.85
$\bar{F}_H - \frac{F^0{}_{H_2}}{2}$ (cal./g. atom)	− 2680	− 1990	− 1640	− 1370	− 1070	− 671	− 183
$\bar{H}_H - \frac{H^0{}_{H_2}}{2}$ (cal./g. atom)	− 7790	− 7890	− 8170	− 8280	− 8600	− 8680	− 8690
$\bar{S}_H - \frac{S^0{}_{H_2}}{2}$ (e.u./g. atom)	− 8.75	− 10.12	− 11.21	− 11.85	− 12.92	− 13.74	− 14.59
$\bar{F}_V - F^0{}_V$ (cal./g. atom)	− 58	− 112	− 161	− 219	− 304	− 456	− 684
$\bar{H}_V - H^0{}_V$ (cal./g. atom)	+ 2	+ 19	+ 60	+ 88	+ 171	+ 196	+ 202
$\bar{S}_V - S^0{}_V$ (e.u./g. atom)	+ 0.11	+ 0.22	+ 0.38	+ 0.53	+ 0.81	+ 1.11	+ 1.51

[a] These data are for **1** g. atom of alloy.

concentration studied, using the same slope as that exhibited by the curve at the lowest concentrations. While this procedure is arbitrary and undoubtedly introduces some uncertainty into the computed thermodynamic quantities, it seems to be the best that can be done in view of the complex nature of the dependence of vapor pressure on composition in the dilute solutions. Actually the uncertainty introduced is slight unless the behavior in the extrapolated region differs by a very large amount (one or two orders of magnitude in $\sqrt{P}/H_N$) from that assumed in the extrapolation.

Discussion of Results

Comparison of the results obtained in the present study with those of Kirschfeld and Sieverts[4] shows poor agreement, their solubilities being much less than those observed in the present study. The disagreement is not surprising, though, considering the low purity of the vanadium (93.2%) used by Kirshfeld and Sieverts, and the well known reduction[3] of hydrogen solubility by interstitial impurities.

The vanadium–hydrogen results resemble in a general way those obtained in the earlier study[3] of the tantalum–hydrogen system. However, upon detailed scrutiny they appear to be somewhat simpler in nature. This is the case despite the failure of the system to conform strictly to Sievert's Law at any of the temperatures studied. Examination of the data shows significant departures from Sievert's Law behavior in all composition ranges. The departures are, however, small at the highest temperature (456°) but increase with decreasing temperature. For a particular isotherm $\sqrt{P}/N_H$ diminishes with increasing hydrogen content in the composition range 2 to 25 atomic %, but at higher concentrations this ratio increases. Similar isotherms have been found for other exothermal occluders, *e.g.*, palladium[7] and zirconium,[8] at temperatures just above the range in which the transition from metal hydride to solid solution occurs. The increase in $\sqrt{P}/N_H$ for values of $N_H > 0.25$ is very simply interpreted. It is due to a falling partial molal entropy of hydrogen in this range, not to a diminished partial heat of vaporization (see Table II). With increasing concentration the number of sites accessible to added hydrogen diminishes and its partial molal entropy sharply decreases. This contributes to the increase in the partial molal free energy of hydrogen and causes a more rapid rise in vapor pressure as N_H is increased than would otherwise be the case. The falling entropy more than compensates for the increased heat of vaporization in the most concentrated solutions studied. The rise in $\sqrt{P}/H_N$ as the hydrogen content of the system is reduced below 20 atomic % is a consequence of the fall of the heat of vaporization with increasing dilution. Down to about 2 atomic % escape is energetically easier the higher the dilution. The reversal in trend at this point is brought about by a change in the dependence of heat of vaporization on composition. Instead of continuing to fall it begins to rise and increases by about 1% as the hydrogen content is reduced from 2 to 0.5%. The fall in $\sqrt{P}/N_H$ reflects this rise in heat of vaporization.

Since the deviations from Sieverts' Law in all but the very concentrated solutions seem to be due to the way in which the heat of vaporization depends on composition, it is now appropriate to attempt to account for the observed composition dependence of this quantity. The behavior which is observed seems to be completely in accordance with what would be expected from qualitative considerations. If the vanadium–hydrogen system is like many other transition metal–hydrogen systems, its unit cell is expanded steadily as hydrogen is introduced into it. Hence the interstitial site in which the hydrogen resides is enlarged as the hydrogen content is increased. It seems reasonable to suppose that this would reduce the energy of the interstitial atom and hence raise its heat of vaporization. Thus one expects a heat of vaporization which increases as N_H increases. However, as has been indicated above, the gradual decrease of the heat of vaporization with dilution is reversed when N_H is reduced below 0.02. This means that the hydrogens exist in unexpectedly low energy states at the highest dilutions. It is tempting to attribute this to the preferential occupancy by the solute atoms of atypical sites, that is, sites that are other than the customary interstitial

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(7) L. J. Gillespie and L. S. Galstaun, THIS JOURNAL, **58**, 2565 (1936).

(8) M. N. A. Hall, S. L. H. Martin and A. L. G. Rees, *Trans. Faraday Soc.*, **41**, 306 (1945).

sites in the metal and in which the hydrogen has exceptionally low energy. Experiment shows[9] that the solvent power of a metal for hydrogen is enhanced by cold working. This undoubtedly results from the retention of atypical sites in the deformed metal which are energetically more favorable for hydrogen than those in the ideal lattice. Clearly no metal will be entirely free of such effects. Atypical sites will exist in any disturbed region in the lattice-at grain boundaries, along dislocations, adjacent to impurities, etc.

With this viewpoint in mind the following sequence of events may be postulated. As the vanadium is hydrogenated, the low-energy, atypical sites will tend to be occupied first. This will lead to a higher than "normal" heat of vaporization at high dilutions. However, as the amount of hydrogen is increased, the atypical sites become saturated and hydrogen will begin to enter the usual lattice sites and the normal trend for the heat of vaporization sets in. Of course, when there is preferential occupancy of sites, this is at the expense of the entropy of the system and will tend to be discouraged the higher the temperature. For this reason and also because the importance of the heat of vaporization in comparison with the entropy of vaporization diminishes as temperature increases, the maxima in the isotherms in Fig. 1 are expected to become less pronounced the higher the temperature. This expectation is borne out by experiment.

These considerations are, of course, relevant to the extrapolation procedure used to evaluate the thermodynamic properties of the system. They suggest that if data for the dissolving of hydrogen in "ideal" vanadium were desired, extrapolation should be made without regard to the fall in $\sqrt{P}/N_H$ at the highest dilutions. It is not exactly clear how one would make such an extrapolation but regardless of how this might be done, it appears that the thermodynamic properties so computed would not differ greatly from those obtained in the present work, except for the most dilute solutions.

Another idea has been advanced to account for deviations from Sieverts' Law such as have been observed for the present system at hydrogen concentrations between 2 and about 25 atomic %. For the Pd–H and Zr–H systems the negative departures from Sieverts' Law have been attributed to attractive interactions between neighboring hydrogen atoms and these systems have been treated on this basis by statistical mechanical methods by Lacher[10] and Rees.[11] If the attractive interactions are the dominant factor, one expects a clustering of solute atoms at low temperatures. The tendency for clustering is of course reduced as the temperature increases with the result that deviations from ideality are diminished correspondingly. Concurrently the destruction of the clusters produces a decrease in the heat of vaporization. Thus if the negative deviations originate with attractive interactions, one expects a significant change in the heat of vaporization with temperature, provided that the temperature range covered is large enough to produce an appreciable change in the magnitude of the observed deviations. This condition is fulfilled in the present study and the data show that within the limit of experimental error the heat of vaporization is invariant with temperature. Furthermore, if the solute atoms interact attractively, one expects the strongest dependence of heat of vaporization on composition to occur in the most concentrated solutions. Actually the converse is found to be the case. The heat of vaporization begins to level off when N_H is increased above about 0.25. Thus the observed behavior does not seem to be in accordance with that expected if attractive interactions between hydrogen atoms were the predominant factor.

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(9) D. P. Smith, "Hydrogen in Metals," University of Chicago Press, Chicago, Ill., 1948, p. 21.

(10) J. R. Lacher, *Proc. Roy. Soc.* (*London*), **A161**, 525 (1937).

(11) A. L. G. Rees, *Trans. Faraday Soc.*, **50**, 335 (1954).

PITTSBURGH, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY DIVISION OF ARGONNE NATIONAL LABORATORY]

Thermodynamics of the Sulfate Complexes of Thorium[1]

BY A. J. ZIELEN

RECEIVED APRIL 17, 1959

By use of the cation-exchange resin technique in perchloric acid solutions at an ionic strength of 2.00 and 25°, thorium(IV) was observed to associate with sulfate according to the stepwise reactions: $Th^{+4} + HSO_4^- = ThSO_4^{+2} + H^+$ and $ThSO_4^{+2} + HSO_4^- = Th(SO_4)_2 + H^+$ with the association constants $K_1 = 166 \pm 8$ and $K_2 = 21.7 \pm 1.5$. The heats and entropy changes of the reactions were determined calorimetrically with the results: ΔH_1 and ΔH_2 equal -0.54 ± 0.05 and -0.89 ± 0.08 kcal./mole, respectively and ΔS_1 and ΔS_2 equal 8.4 ± 0.2 and 3.2 ± 0.3 cal. deg.$^{-1}$ mole^{-1}, respectively. The heat of ionization of bisulfate ion at an ionic strength of 2.00 and 25° was also measured calorimetrically with the result ΔH equals -5.54 ± 0.17 kcal./mole.

Introduction

The complexing of aqueous thorium by inorganic ligands has received considerable attention in recent years,[2] but certain aspects have been neglected. A cursory examination of the literature has failed to reveal a single determination of the heats and entropies of complexing, and in addition nearly all complexing constants have been determined by

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(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) H. W. Dodgen and G. K. Rollefson, THIS JOURNAL, **71**, 2600 (1949); (b) R. A. Day and R. W. Stoughton, *ibid.*, **72**, 5662 (1950); (c) E. L. Zebroski, H. W. Alter and F. K. Heumann, *ibid.*, **73**, 5646 (1951); (d) W. C. Waggener and R. W. Stoughton, *J. Phys. Chem.*, **56**, 1 (1952); (e) V. V. Fomin and E. P. Maiorova, *Zhur. Neorg. Khim.*, **1**, 1703 (1956).