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Thermodynamics of Solid Solution of Hydrogen in Ta_6S and $Nb_{21}S_8$*

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Equilibrium hydrogen pressures in the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 have been measured for temperatures in the range 300–550°C. Data for five different temperatures were treated to obtain various thermodynamic quantities. The reactions $H(S.S.) = \frac{1}{2}H_2(g)$ for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 are found to be less endothermic than the respective metal–hydrogen reactions. Standard entropies of dissolved hydrogen in the sulfides are similar to those of hydrogen in the metals.

Introduction

During the past several years there has been a number of investigations of the solid solution of hydrogen in the group V bcc transition metals V, Nb, and Ta (*1–7*). Thermodynamic data thus obtained have been the subject of several theoretical and structural interpretations regarding the nature of solid solutions of hydrogen in the bcc metals (*8*, *9*). In the bcc metals there are 12 tetrahedral and 6 octahedral sites per unit cell, thus permitting the formula MH_9 for the maximum composition of the hydride (*10*). However, the highest hydride so far realized in the bcc metals has the formula MH_2; thus, the interpretation of various thermodynamic quantities, particularly the entropy data, have suffered from uncertainties that are related to the question of the interstitial sites available to the hydrogen atoms. To resolve these difficulties it has been argued that hydrogen in a given site essentially blocks the neighboring interstitial sites from being occupied by hydrogen atoms (*11*).

There are four known metallic compounds of the group V metals which consist of greater than $66\frac{2}{3}$ at% metal; namely, V_3S, $Nb_{14}S_5$, $Nb_{21}S_8$, and Ta_6S. These compounds have structures different from each other and from the metals from which they derive. Thus, α-V_3S has a tetragonal structure; $Nb_{21}S_8$ and $Nb_{14}S_5$ have complex structures, based upon cubic coordination of the niobium atoms and capped trigonal prismatic coordination of the sulfur atom, whereas Ta_6S has a structure of particular interest in that it can be described as chains of body-centered pentagonal antiprisms of Ta atoms sharing faces in one direction and interconnected via sulfur atoms in the other two directions. These structures have been recently discussed (*12*). The structural variety exhibited by the subsulfides of the group V elements makes the investigation of their interactions with hydrogen most interesting. Further, the results of

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these studies will provide a direct comparison of the thermodynamics of hydrogen interactions in these compounds with those in the bcc metals. In this paper we report the results of hydrogen interaction with Ta_6S and $Nb_{21}S_8$.

Experimental

Materials. Powdered metals (99.99%) used for the synthesis of Ta_6S and $Nb_{21}S_8$ were obtained by the thermal decomposition of their respective hydrides under a continuous vacuum at temperatures around 850–900°C. For preparation of metal hydride it was found advantageous to use metal chips rather than rod or sheet. Synthesis of the subsulfides, Ta_6S and $Nb_{21}S_8$, was accomplished by a low-temperature reaction of the stoichiometric mixture between 700 and 800°C in an evacuated Vycor tube for 2 to 3 days, followed by induction heating to around 1300°C for 3 hr in a tungsten crucible. Samples were characterized by Guinier powder patterns and metallographic examinations along with combustion analysis for sulfur.

Apparatus. A schematic diagram of the gas volumetric apparatus is shown in Fig. 1. The effective volumes of the systems were calibrated with increasing furnace temperature so that the composition of the solid phase could be calculated from a change in the ambient hydrogen pressure. The quartz furnace tube was about 15 mm in diameter and extended into a stainless steel block kept at the middle of the furnace. This device ensured a homogeneity in temperature over a distance of about 5.5 cm and the temperature of the furnace was constant to within ±2°C. The manometer used could be read to ±0.3 mm. Samples to be hydrided were placed inside the furnace tube in a platinum boat. The samples were outgassed for about 4 hr at 850–900°C and hydrogen was introduced. The sample temperature was slowly cooled to about 400°C and held at that value overnight, and the sample was then reheated to higher temperature and evacuated. This procedure was repeated several times in order to fully activate the sample. The maximum hydrogen compositions obtained yielded formulas close to Ta_6SH_2 and $Nb_{21}S_8H_5$.

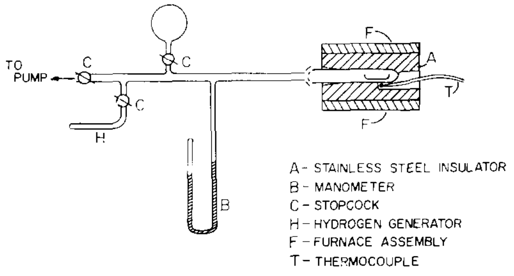

FIG. 1. Schematic diagram of the equilibration apparatus.

Several hydrided specimens were analyzed for hydrogen by a hot vacuum extraction technique (*13*). The total hydrogen content of the sample was determined from the measurement of the pressure of the gas collected in a known volume. This gave a check on the reproducibility of the composition of the hydride phase obtained using the gas volumetric apparatus as described earlier.

Characterization of hydrided specimens. Hydrogen containing phases of $Nb_{21}S_8$ and Ta_6S were examined by Guinier powder patterns and metallography. These examinations showed that no new phase was obtained by the action of hydrogen on Ta_6S and $Nb_{21}S_8$ in the temperature and pressure region investigated. Thus, hydrogen dissolved in the subsulfides $Nb_{21}S_8$ and Ta_6S, forming solid solutions (see later).

Calculation of thermodynamic quantities. Measurements of partial pressures of hydrogen at various temperatures over a range of compositions provide a basis for the calculation of partial thermodynamic quantities for hydrogen in the solid phase. At equilibrium, the chemical potential of $H_2(g)$ and H(S.S.) are related by

$$\mu_{H(S.S.)} = \tfrac{1}{2}\mu_{H_2(g)}.$$

That is,

$$\mu_{H(S.S.)} = \tfrac{1}{2}\mu^{\circ}_{H_2(g)} + \tfrac{1}{2}RT\ln P_{H_2}$$

with the ideal gas approximation. The partial molar free energy of hydrogen in solid solution relative to the ideal gas standard state thus can be determined from measurements of hydrogen pressure. Similarly, the relative partial molar enthalpy $\{\bar{H}_{H(S.S.)} - \frac{1}{2}\bar{H}^{\circ}_{H_2(g)}\}$ and the entropy $\{\bar{S}_{H(S.S.)} - \frac{1}{2}\bar{S}^{\circ}_{H_2(g)}\}$ may be calculated for any given composition. If the hydrogen solid solution follows Sievert's law, the equilibrium constant K appropriate to the gas–solid reaction may be written as

$$K = P_{H_2}^{1/2}/N_H,$$

where N_H is the mole fraction of atomic hydrogen in the solid. The changes in the standard free energy, enthalpy, and entropy for the solution reaction may be calculated. The equilibrium constants K, which are the limiting slopes at low N_H of the $P_{H_2}^{1/2}$ vs N_H curves have been obtained for temperatures in the range 300–550°C for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2. ΔH° values for the reaction $H(S.S.) = \frac{1}{2}H_2(g)$ have been calculated from the slope of the $\log K$ vs $(1/T)^{\circ}K^{-1}$ plot and $\Delta G^{\circ} = -RT\ln K$. From the knowledge of ΔG° and ΔH°, the standard entropies of reaction ΔS° have been calculated. Since the entropy of gaseous H_2 is known at various temperatures, it was also possible to calculate the entropy $\bar{S}^{\circ}_{H(S.S.)}$ of atomic hydrogen in the solid solution standard state.

Results and Discussion

In studies of metal hydrogen systems, hysteresis has been frequently found to occur in the isothermal pressure–composition behavior. In the tantalum and niobium sulfide–hydrogen systems, no such hysteresis phenomenon was observed. Therefore, it can be concluded that the dissociation pressures obtained in these studies represent equilibrium data.

Experimental hydrogen pressure data for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 are shown in Figs. 2 and 3. For clarity, data for three temperatures are shown for each of the systems. Equilibrium hydrogen pressures for some rounded compositions for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 are presented in Tables I and II. Since X-ray and metallographic examinations of the product of interaction of hydrogen with the subsulfides of tantalum and niobium did not show evidence of any ternary phase, equilibrium vapor pressure data were plotted as $P_{H_2}^{1/2}$ vs N_H for temperatures from 300–550°C for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2. An examination of the plots obtained for the five different

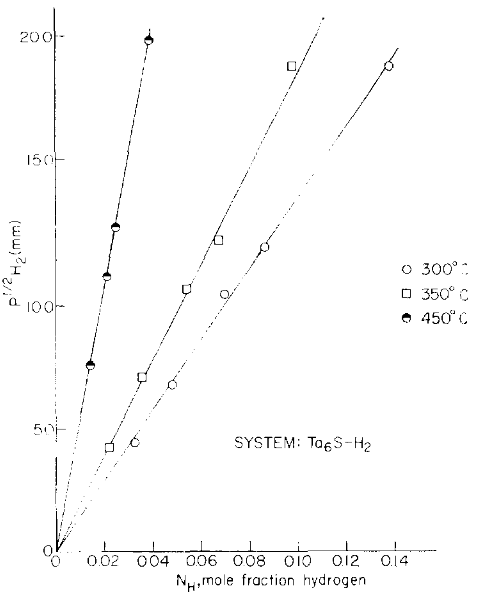

FIG. 2. Pressure–composition isotherms for tantalum sulfide (Ta_6S)–hydrogen system.

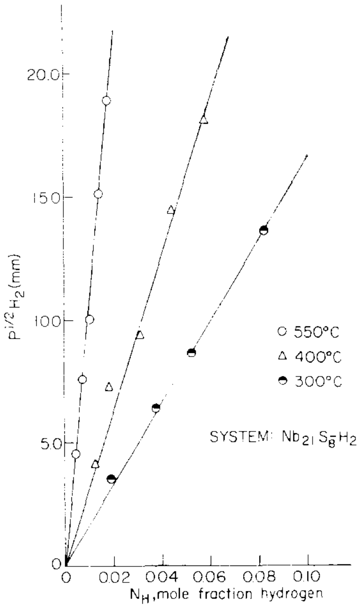

FIG. 3. Pressure–composition isotherms for niobium sulfide ($Nb_{21}S_8$)–hydrogen system.

TABLE I

EQUILIBRIUM HYDROGEN PRESSURES FOR THE TANTALUM SULFIDE (Ta_6S)–HYDROGEN SOLID SOLUTION

Composition,	P (mm of Hg) at				
N_H	300°C	350°C	400°C	450°C	550°C
0.010	1.90	3.20	9.30	26.20	65.35
0.020	7.80	14.80	39.40	103.10	315.65
0.030	17.55	34.70	90.30	230.10	—
0.040	31.20	63.0	161.90	408.80	—
0.060	70.30	144.80	367.50	—	—
0.080	125.0	260.1	—	—	—
0.100	195.40	—			
0.120	281.45	—			
0.140	383.10	—			

TABLE II

EQUILIBRIUM HYDROGEN PRESSURES FOR THE NIOBIUM SULFIDE ($Nb_{21}S_8$)–HYDROGEN SOLID SOLUTION

Composition,	P (mm of Hg) at				
N_H	300°C	350°C	400°C	450°C	550°C
0.010	2.60	4.30	9.70	25.30	108.45
0.020	10.30	17.30	38.90	101.15	433.90
0.030	23.25	39.0	87.50	227.55	—
0.040	41.30	69.30	155.55	404.55	—
0.060	93.0	156.0	350.0	—	
0.080	165.30	—			
0.100	258.3	—			

temperatures for these systems show that they obey Sievert's law. Therefore, Ta_6S and $Nb_{21}S_8$ form ideal solid solutions with hydrogen in the specified composition ranges.

Enthalpy. Relative partial enthalpies were obtained for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 for temperatures 300–550°C with varying concentration of hydrogen and are given in Tables III and IV. An examination of the relative partial enthalpies, $\{\bar{H}_{H(s.s.)} - \frac{1}{2}\bar{H}^{\circ}_{H_2(g)}\}$ for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 shows that there is a close similarity between the enthalpies of solution of these systems. A comparison of the thermodynamics of solid solutions of hydrogen in bcc niobium and tantalum reveals a marked similarity between the enthalpies of solution of hydrogen in niobium and tantalum. For example, at hydrogen mole fraction, $N_H = 0.020$; the relative partial molar enthalpy values are 8.8 and 8.5 kcal/mole H for the systems Nb–H and Ta–H at 340 and 330°C, respectively (*8*). The Ta_6S–H_2 and $Nb_{21}S_8$–H_2 solutions and the hydrogen solutions of the respective metals exhibit an energetic similarity in spite of marked structural differences between the sulfides and the metals. However, the partial molar enthalpies of solution of hydrogen in Ta_6S–H_2 and $Nb_{21}S_8$–H_2 systems are slightly less exothermic (about 1.5 kcal less) than those of the respective metals. Further, for the binary metal–hydrogen systems, Ta–H and Nb–H, there is apparently a slight increase in the magnitudes of the partial enthalpies with increasing hydrogen concentrations of the solid. On the other

TABLE III

PARTIAL MOLAR THERMODYNAMIC FUNCTIONS FOR HYDROGEN IN TANTALUM SULFIDE (Ta_6S)–HYDROGEN SOLID SOLUTION

Composition, N_H	$\bar{H}_{H(s.s.)}-\frac{1}{2}H^{\circ}_{H_2(g)}$ (kcal/g-atom H)	$\bar{S}_{H(s.s.)}-\frac{1}{2}S^{\circ}_{H_2(g)}$ (e.u.)	$\bar{\mu}_{H(s.s.)}-\frac{1}{2}\mu^{\circ}_{H_2(g)}$[a] (kcal/g-atom)
0.010	7.0 ± 0.6	6.1 ± 0.8	−2.94
0.020	7.2 ± 0.4	7.9 ± 0.5	−1.97
0.030	7.1 ± 0.6	8.7 ± 1.0	−1.42
0.040	7.0 ± 0.6	9.2 ± 1.0	−1.03
0.060	6.2 ± 0.7	8.7 ± 1.2	−0.48

[a] Data at 400°C.

TABLE IV

PARTIAL MOLAR THERMODYNAMIC FUNCTIONS FOR HYDROGEN IN NIOBIUM SULFIDE ($Nb_{21}S_8$)–HYDROGEN SOLID SOLUTION

Composition, N_H	$\bar{H}_{H(S.S.)}-\frac{1}{2}H^\circ_{H_2(g)}$ (kcal/g-atom H)	$\bar{S}_{H(S.S.)}-\frac{1}{2}S^\circ_{H_2(g)}$ (e.u.)	$\bar{\mu}_{H(S.S.)}-\frac{1}{2}\mu^\circ_{H_2(g)}$[a] (kcal/g-atom)
0.010	7.1 ± 0.6	6.9 ± 0.9	−2.91
0.020	7.1 ± 0.6	8.3 ± 0.9	−1.98
0.030	6.2 ± 0.9	7.5 ± 1.3	−1.44
0.040	6.2 ± 0.9	8.0 ± 1.3	−1.06
0.060	5.0 ± 0.8	6.7 ± 1.4	−0.51

[a] Data at 400°C.

TABLE V

STANDARD THERMODYNAMIC FUNCTIONS FOR THE REACTION $H(S.S.) = \frac{1}{2}H_2(g)$ FOR THE TANTALUM SULFIDE (Ta_6S)–HYDROGEN SOLID SOLUTION

T (°C)	Equilibrium constant (K)	ΔG° (cal/g-atom)	ΔH° (cal/g-atom)	ΔS° (e.u.)	$\bar{S}^\circ_{H(S.S.)}$ (e.u.)	$\bar{S}^\circ_H$ for H in Ta metal (e.u.)
300	5.0	−1832		16.0	2.0	3.3
350	7.4	−2478		15.7	2.2	3.3
400	11.6	−3278	7360 ± 300	15.8	2.7	3.9
450	18.2	−4168		15.9	2.5	—
550	35.1	−5819		16.0	3.0	—

TABLE VI

STANDARD THERMODYNAMIC FUNCTIONS FOR THE REACTION $H(S.S.) = \frac{1}{2}H_2(g)$ FOR THE NIOBIUM SULFIDE ($Nb_{21}S_8$)–HYDROGEN SOLID SOLUTION

T (°C)	Equilibrium constant (K)	ΔG° (cal/g-atom)	ΔH° (cal/g-atom)	ΔS° (e.u.)	$\bar{S}^\circ_{H(S.S.)}$ (e.u.)	$\bar{S}^\circ_H$ for H in Nb metal (e.u.)
300	5.8	−2007		15.8	2.1	2.1
350	7.5	−2502	7100 ± 600	15.4	2.6	1.9
400	11.3	−3244		15.3	3.2	2.5
450	18.2	−4172		15.5	3.0	2.5
550	37.7	−5940		15.8	3.2	—

hand, partial enthalpies of hydrogen in Ta_6S and $Nb_{21}S_8$ appear to decrease in magnitude with increasing concentration of hydrogen in the solid phase. The heats of reaction, ΔH° for the reaction $H(S.S.) = \frac{1}{2}H_2(g)$ have been obtained for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 from the respective plots of logarithm of equilibrium constants, K vs $(1/T)°K^{-1}$ (Tables V and VI) which are plotted in Fig. 4. It is seen that ΔH° for the above reaction for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 are about 7.4 and 7.1 kcal, respectively. Calculations of ΔH° for the reaction $H(S.S.) = \frac{1}{2}H_2(g)$ for the Ta– and

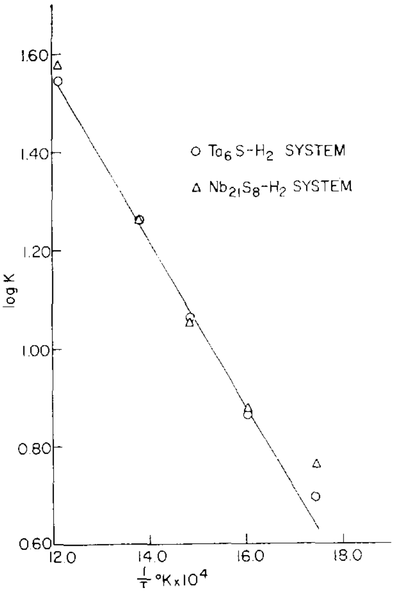

FIG. 4. Logarithm of equilibrium constants vs reciprocal temperature.

Nb–hydrogen systems from literature (*1*, *3*) yielded values of 9.0 and 10.6 kcal, respectively. Thus, it is seen that the formation of these lower sulfides slightly diminishes the exothermicity of the metal–hydrogen interaction.

Entropy. Relative partial entropies of hydrogen $\{\bar{S}_{\mathrm{H(S.S.)}} - \frac{1}{2}S^{\circ}_{\mathrm{H_2(g)}}\}$, for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 have been calculated for different hydrogen concentrations and are given in Tables III and IV. ΔS° for the reaction $H(S.S.) = \frac{1}{2}H_2(g)$ has also been calculated for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 (Tables V and VI). Using the entropy of gaseous H_2 (*14*), the standard entropy of dissolved hydrogen, $\bar{S}^{\circ}_{\mathrm{H(S.S.)}}$ has been calculated for the systems Ta_6S–H_2 and $Nb_{21}S_8$–H_2 (Tables V and VI). Similarly, $\bar{S}^{\circ}_{\mathrm{H(S.S.)}}$ for the metals Ta and Nb have been calculated from data obtained from literature (*1*, *3*) and are shown in Tables V and VI. An examination of the values for $\bar{S}^{\circ}_{\mathrm{H(S.S.)}}$ in Ta_6S and $Nb_{21}S_8$ shows that the standard entropies of dissolved hydrogen in these subsulfides are similar to those of the respective metals. It is known that hydrogen diffusion (*8*) in the bcc vanadium, niobium, and tantalum are very fast, with diffusion constants at 300–400°C of 10^{-4} to 10^{-5} cm^2/sec. High mobility of hydrogen in these subsulfides has been confirmed from a preliminary NMR measurement (*15*).

Conclusions

There are three conclusions based on the observations reported above. The first is that the enthalpies and entropies of solution of hydrogen in these solid solvents are not strongly structure dependent. The second is that the enthalpies of reaction to form solid solutions of hydrogen from gaseous hydrogen and solid solvent are slightly less exothermic in the cases of these metal–rich sulfides than in the cases of the elements. The third conclusion is that the above in turn suggest that the interactions of hydrogen in the solid solutions can be viewed as interactions between hydrogen and Ta or Nb as opposed to interactions between hydrogen and a structural unit, and that sulfur and hydrogen are in competition with respect to interactions with the metal atoms. It is thus indicated by the data that hydrogen is weakly electronegative relative to the metallic elements.

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