

## Thermodynamics of Solid Solution of Hydrogen in $M_2C$ Type Carbides of Vanadium and Niobium†

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Equilibrium hydrogen pressures in the systems  $V_2C-H_2$  and  $Nb_2C-H_2$  have been determined at several temperatures in the range 400–650°C. Hydrogen pressure data were treated to obtain various thermodynamic quantities for the solutions of hydrogen in  $V_2C$  and  $Nb_2C$ . It has been found that the enthalpies of the reaction  $H(S.S.) = \frac{1}{2}H_2(g)$  are similar but slightly less endothermic compared to the respective metal hydrogen solid solutions. Entropies of dissolved hydrogen in  $V_2C$  and  $Nb_2C$  are also found to be similar to those of hydrogen in the respective metals.

### Introduction

An investigation of the thermodynamics of solid solutions of hydrogen in  $Ta_6S$  and  $Nb_{21}S_8$  (1) revealed that despite marked structural differences between the subsulfides and the metals, the entropies of the solution reactions of hydrogen in  $Ta_6S$  and  $Nb_{21}S_8$  are similar to each other and to those of the metals. The enthalpies of the solution reactions in the subsulfides have been found to be similar but slightly less exothermic compared to the respective metals. Further,  $Ta_6S$  and  $Nb_{21}S_8$  were found to be poorer solvents for hydrogen when compared with the metals.

Metal rich sulfides, carbides, and phosphides of Group V metals crystallize in a variety of structures. Some of these structures have been recently discussed (2). The various metallic compounds of Group V metals, e.g.,

$V_3S$ ,  $Nb_{21}S_8$ ,  $Ta_6S$ ,  $V_3P$ ,  $Nb_{14}S_5$ ,  $V_2C$ ,  $Nb_2C$ , etc., exhibit structures which are generally different from each other and from the metals from which they are derived. All of these compounds except  $V_2C$  and  $Nb_2C$  have complex structures. The  $M_2C$  carbides of vanadium and niobium crystallize with hexagonal  $L'_3$  type structure (3). The structural variety exhibited by these compounds makes the investigation of their hydrogen interactions most interesting. Studies of hydrogen interactions in these compounds will provide information concerning the effect of crystal structure on  $\Delta S^\circ$  and  $\Delta H^\circ$  of solution. In this context, the results of hydrogen solution in the compounds  $Ta_6S$  and  $Nb_{21}S_8$  have been described (1). Preliminary investigations of the hydrogen interactions in several of the metal-rich compounds, e.g.,  $\alpha-V_3S$ ,  $V_3P$ ,  $V_2C$ ,  $Nb_2C$ , and  $Ta_2C$ , indicate that they form solid solutions with hydrogen. Peterson and Rexer (4) investigated the hydrogen interactions in a number of metal-rich carbides and reported

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the formation of ternary compounds with a hexagonal structure and of approximate stoichiometry  $MC:MH_x$  (where  $M = \text{Ti, Zr, Hf, Y, La}$ ).

This paper reports the results on the equilibrium hydrogen pressure measurements on the hexagonal dimetallic carbides of vanadium and niobium.

### Materials

The compounds  $V_2C$  and  $Nb_2C$  to be equilibrated with hydrogen were prepared by arc-melting the respective metals (99.99%) with weighed amounts of graphite in the form of spectroscopic rods. In the case of  $Nb_2C$ , it was found necessary to anneal the arc-melted specimen at 1800–1900°C in order to get a homogeneous product. High-temperature annealing was done in an inductively heated tungsten crucible. Samples were characterized by Debye–Scherrer powder patterns along with combustion analysis for carbon. The compositions of the vanadium and niobium carbides used for equilibrium hydrogen pressure measurements were  $V_2C_{0.97}$  and  $Nb_2C$ , respectively.

The apparatus used for hydrogen pressure measurements has already been described (1). Samples of  $V_2C$  or  $Nb_2C$  were contained in a platinum boat and were outgassed for several hours at about 850–900°C. Hydrogen from the thermal decomposition of uranium hydride was introduced into the system with the sample at about 900°C; the sample was then cooled to about 400°C over several hours. The system was then reheated to high temperature and evacuated. This procedure was repeated several times, after which equilibrium hydrogen pressure measurements were made. X-ray powder patterns of the hydrided specimen show that hydrogen dissolves in  $Nb_2C$  and  $V_2C$ , forming no new phase.

### Calculation of Thermodynamic Quantities

X-ray diffraction patterns of the hydrided specimen show that hydrogen forms solid solutions in  $V_2C$  and  $Nb_2C$ . Therefore, equilibrium hydrogen pressure data could be treated to obtain different thermodynamic

functions for hydrogen in the solid. The methods of calculation for different quantities have been described previously (1). At equilibrium, the chemical potential of  $H_2(g)$  and  $H(S.S.)$  are related by

$$\mu_{H(S.S.)} = \frac{1}{2}\mu_{H_2(g)} + \frac{1}{2}RT \ln P_{H_2}$$

with the ideal gas approximation. Therefore, measurements of hydrogen pressure will provide a basis for the calculation of both relative partial molar quantities and the standard thermodynamic functions of hydrogen in the solid.

### Results and Discussion

In the metal carbide–hydrogen studies it has been found that the time of equilibration was relatively longer than in the case of the sulfides. It took several days for the products to reach equilibrium. The equilibrium was obtained by both absorption and desorption of hydrogen. Experimental hydrogen pressure data at several temperatures in the range 400–650°C have been determined for the systems  $V_2C-H_2$  and  $Nb_2C-H_2$ . For clarity, data for three temperatures are shown in Figs. 1 and 2. Hydrogen pressure data for some rounded compositions obtained by least-squares treat-

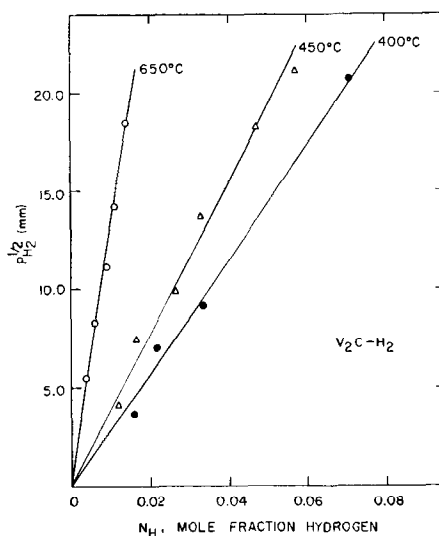


FIG. 1. Pressure-composition isotherms for vanadium carbide ( $V_2C$ )-hydrogen system.

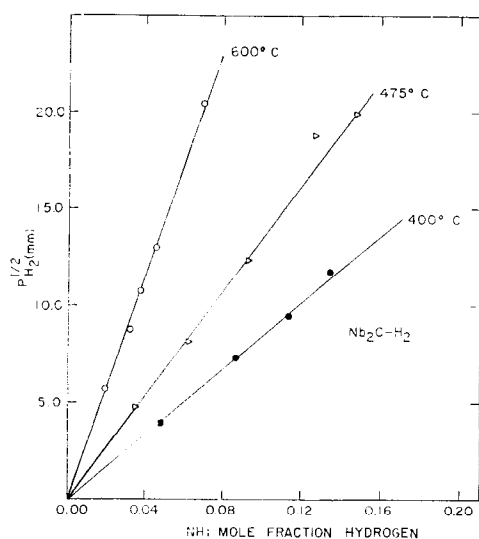


FIG. 2. Pressure-composition isotherms for niobium carbide ( $Nb_2C$ )-hydrogen system.

TABLE I

EQUILIBRIUM HYDROGEN PRESSURES FOR THE VANADIUM CARBIDE ( $V_2C$ )-HYDROGEN SOLID SOLUTION

Composition, $N_H$	$P$ (mm Hg) at:				
	400°C	450°C	550°C	600°C	650°C
0.010	8.15	16.15	58.35	101.3	166.7
0.015	18.50	34.85	113.0	230.15	372.0
0.020	34.0	60.65	185.6	411.0	—
0.040	132.5	234.5	—	—	—

TABLE II

EQUILIBRIUM HYDROGEN PRESSURES FOR THE NIOBIUM CARBIDE ( $Nb_2C$ )-HYDROGEN SOLID SOLUTION

Composition $N_H$	$P$ (mm Hg) at:			
	400°C	475°C	550°C	600°C
0.010	0.6	1.6	6.5	7.6
0.030	6.3	16.5	55.8	74.0
0.050	18.0	46.9	153.5	208.6
0.070	35.7	92.8	299.5	411.6
0.10	73.5	190.7	—	—

ment of experimental points are presented in Tables I and II. Sievert's plots for the different temperatures for the systems  $V_2C-H_2$  and  $Nb_2C-H_2$  (Figs. 1 and 2) show that they obey Sievert's law. This would indicate that hydrogen forms ideal solid solutions with  $V_2C$  and  $Nb_2C$  up to the composition studied.

### Enthalpies

Relative partial molar enthalpies for the solutions of hydrogen in  $V_2C$  and  $Nb_2C$  at various concentrations are presented in Tables III and IV, respectively. A comparison of the relative partial enthalpies  $\{\bar{H}_{H(s.s.)} - \frac{1}{2}H_{H_2(g)}^\circ\}$  for the systems  $V_2C-H_2$  and  $Nb_2C-H_2$  at a given hydrogen concentration shows that the partial enthalpies for the system  $Nb_2C-H_2$  are slightly higher than those of the  $V_2C-H_2$  system. Enthalpies of solution of hydrogen in bcc niobium are reported to be higher in

TABLE III

PARTIAL MOLAR THERMODYNAMIC FUNCTIONS FOR THE VANADIUM CARBIDE ( $V_2C$ )-HYDROGEN SOLID SOLUTION

$N_H$	$\{H_{H(s.s.)} - \frac{1}{2}H_{H_2(g)}^\circ\}$ (kcal/mole H)	$\{S_{H(s.s.)} - \frac{1}{2}S_{H_2(g)}^\circ\}$ (cal/kmole H)
0.010	$-7.48 \pm 0.1$	$-6.6 \pm 0.1$
0.015	$-7.45 \pm 0.3$	$-7.3 \pm 0.4$
0.020	$-7.17 \pm 0.6$	$-7.5 \pm 0.8$
0.040	$-5.89 \pm 0.1$	$-7.0 \pm 0.1$

TABLE IV

PARTIAL MOLAR THERMODYNAMIC FUNCTIONS FOR THE NIOBIUM CARBIDE ( $Nb_2C$ )-HYDROGEN SOLID SOLUTION

$N_H$	$\{\bar{H}_{H(s.s.)} - \frac{1}{2}H_{H_2(g)}^\circ\}$ (kcal/mole H)	$\{S_{H(s.s.)}^\circ - \frac{1}{2}S_{H_2(g)}^\circ\}$ (cal/kmole H)
0.010	$-7.87 \pm 0.9$	$-4.5 \pm 1.2$
0.015	$-7.70 \pm 0.7$	$-5.1 \pm 1.0$
0.020	$-7.60 \pm 0.6$	$-5.6 \pm 0.9$
0.040	$-7.50 \pm 0.6$	$-6.9 \pm 0.7$
0.050	$-7.45 \pm 0.5$	$-7.2 \pm 0.7$

TABLE V

STANDARD THERMODYNAMIC FUNCTIONS FOR THE REACTION  $H(S.S.) = \frac{1}{2}H_2(g)$  FOR VANADIUM CARBIDE ( $V_2C$ )-HYDROGEN SOLID SOLUTION

$T$ ( $^{\circ}C$ )	$\Delta\bar{G}^{\circ}$ (cal/g·atom)	$\Delta\bar{H}^{\circ}$ (cal/g·atom)	$\bar{S}\Delta^{\circ}$ (cal/kmole H)	$S_{H(S.S.)}^{\circ}$ in $V_2C$ (cal/kmole H)	$\bar{S}_{H(S.S.)}^{\circ}$ in V metal (cal/kmole H) (5)	$\bar{S}_{H(S.S.)}^{\circ}$ in V metal (cal/kmole H) (6)
400	-3140		15.6	2.8	4.3 <sup>a</sup>	2.7
450	-3760		15.4	3.1		
		+7380 ±810				
550	-5030		15.0	4.0		
600	-6260		15.6	3.8		
650	-7040		15.6	3.8		

<sup>a</sup> At 434 $^{\circ}C$ .

TABLE VI

STANDARD THERMODYNAMIC FUNCTIONS FOR THE REACTION  $H(S.S.) = \frac{1}{2}H_2(g)$  FOR NIOBIUM CARBIDE ( $Nb_2C$ )-HYDROGEN SOLID SOLUTION

$T$ ( $^{\circ}C$ )	$\Delta\bar{G}^{\circ}$ (cal/g·atom)	$\Delta\bar{H}^{\circ}$ (cal/g·atom)	$\Delta\bar{S}^{\circ}$ (cal/kmole H)	$S_{H(S.S.)}^{\circ}$ in in $Nb_2C$ (cal/kmole H)	$\bar{S}_{H(S.S.)}^{\circ}$ in Nb metal (cal/kmole H) (6)	$\bar{S}_{H(S.S.)}^{\circ}$ in Nb metal (cal/kmole H) (7)
400	-1530		13.2	5.2	4.4 <sup>a</sup>	2.5
		+7370 ±500				
475	-2410		13.0	5.7		
550	-3580		13.3	5.8		
600	-4095		13.1	6.2		

<sup>a</sup> At 444 $^{\circ}C$ .

magnitude at a given concentration compared to those of V, for example at  $N_H = 0.02$  (where  $N_H$  is the atomic fraction of hydrogen in the solid), the partial enthalpies of hydrogen in niobium and vanadium are about 8.8 and 7.7 kcal/mole of H, respectively (5). From Tables III and IV, it is seen that enthalpies of hydrogen solid solutions in  $V_2C$  and  $Nb_2C$  are somewhat lower than the corresponding metals. Thus at  $N_H = 0.02$ , the partial molar enthalpies of solutions of hydrogen in  $Nb_2C$  and  $V_2C$  are 7.6 and 7.1 kcal/mole of H,

respectively. Therefore, formation of carbides by these metals reduces the exothermicity of the metal-hydrogen interactions. In the cases of hydrogen in the metals, the relative partial enthalpies increase in magnitude with concentration in contrast to the decreasing trend observed for the carbides. This behavior is similar to that found for  $Ta_6S-H_2$  and  $Nb_{21}S_8-H_2$  systems. The standard heats of solution of hydrogen in  $V_2C$  and  $Nb_2C$  are found to be similar and are shown in Tables V and VI. The plot of  $\log K$  vs  $1/T$  is presented in Fig. 3.

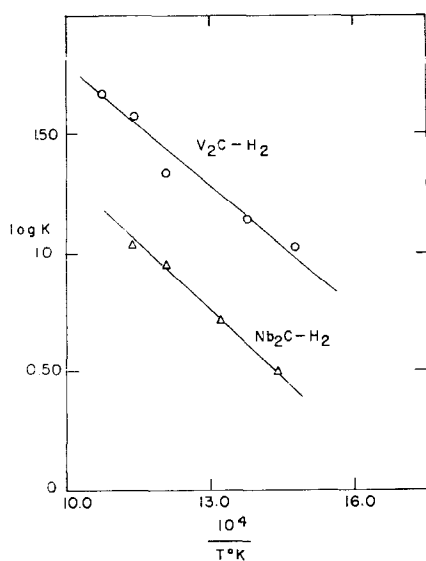


FIG. 3. Logarithm of equilibrium constants vs. reciprocal temperature.

### Entropy

Relative partial entropies of hydrogen for the systems  $V_2C-H_2$  and  $Nb_2C-H_2$  are shown in Tables III and IV.  $\Delta S^\circ$  for the reaction,  $H(S.S.) = \frac{1}{2}H_2(g)$  are presented in Tables V and VI along with the entropy of dissolved hydrogen in  $V_2C$  and  $Nb_2C$  and also for hydrogen in vanadium and niobium metals calculated from Ref. (5)–(7). A comparison of entropies of dissolved hydrogen,  $S_{H(S.S.)}^\circ$ , in  $V_2C$  and  $Nb_2C$  shows that the entropies of hydrogen in the carbides are similar to those observed for the respective metals. A similar observation was made for solutions of hydrogen in  $Ta_6S$  and  $Nb_{21}S_8$ .

### Conclusion

In spite of the marked difference between the structures of the carbides investigated here and

the sulfides previously investigated, the thermodynamic properties of the dissolved hydrogen atoms are decidedly similar. In both cases (the metallic sulfides and the metallic carbides), the compound formation slightly decreases the stability of the dissolved hydrogen relative to gaseous hydrogen principally due to a slight decrease in the energetic stability of the solution. Thus the following model for hydrogen solution in the metal rich compounds seems appropriate. (1) The interaction of the hydrogen is principally an interaction with the electrons in bands formed principally from orbitals centered upon the metal atoms. (2) the hydrogen interacts less effectively in cases in which the number of electrons has been reduced by interaction with a more electro-negative element such as carbon or sulfur. (3) The hydrogen-metal interactions are not markedly altered by compound formation in those cases in which the compound maintains its metallic character by virtue of extensive metal-metal interactions (the metal-rich compounds).

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