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The Higher Hydrides of Vanadium and Niobium[1]

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Vanadium dihydride and niobium dihydride were prepared by the direct reaction of hydrogen with the metal. Attempts to prepare tantalum dihydride were unsuccessful. Pressure–composition isotherms were determined for the systems $VH_{\sim 0.9}$–$VH_{2.0}$ and $Nb_{\sim 0.9}$–$NbH_{2.0}$. Pertinent thermodynamic data were calculated for each system. The phase diagrams for the vanadium–hydrogen system and the niobium–hydrogen system were extended to a composition corresponding to MH_2.

The group Va elements, vanadium, niobium, and tantalum, all react directly with hydrogen at atmospheric pressure and room temperature to form nonstoichiometric monohydrides which have a limiting composition of $MH_{\sim 0.9}$. These hydride systems have been the subject of extensive investigations by several authors.[2] It is also possible to prepare higher hydrides of vanadium and niobium through the direct reaction of the metal with hydrogen or by indirect aqueous and electrolytic techniques. Thus, Maeland, *et al.*,[3a] prepared $VH_{\sim 1.6}$ directly while Brauer and Muller[3b] using an aqueous electrolytic method obtained $NbH_{2.00+x}$. There is no report of the existence of any higher tantalum hydride. Maeland[4] has published a partial phase diagram for the system V–H_2 but the phase boundaries for compositions above $VH_{0.9}$ were only tentative. Thus, apart from the mere fact of their existence very little is known of these systems in the range $MH_{0.9}$–$MH_{2.0}$. We have synthesized the dihydrides of V and Nb by direct combination with hydrogen at high pressure and have examined these systems in terms of pressure, temperature, and composition relationships and have derived from these data appropriate thermodynamic functions and phase boundaries. An attempt to prepare tantalum dihydride by the same method was not successful, only attaining a maximum hydrogen content corresponding to a composition of $TaH_{0.90}$. Since the efforts to obtain tantalum dihydride were unsuccessful, it will not be discussed further except in the Experimental Section.

Experimental Section

Materials.—During the course of this investigation it was found that some properties, especially the dissociation pressure, of the vanadium hydride system (*i.e.*, $VH_{0.95}$–VH_2) were quite sensitive to small amounts of impurities in the initial vanadium sample. Thus, unless noted, all the vanadium experiments were carried out using high-purity, zone-refined vanadium rod obtained from the Materials Research Corp., Orangeburg, N. Y. A typical analysis of this material is shown in Table I. However, for comparison purposes several experiments are described in which commercial grade vanadium was used. The latter was obtained from the Materials Systems Division of the Union Carbide Corp. This vanadium consisted of 4-mesh granules and had an assay of 99.6% vanadium. It contained 430 ppm of oxygen and the major metallic impurities as determined by spectrographic analysis were Fe, Si, Mo, and Ta.

In contrast to the results obtained with vanadium, there were no significant differences in the behavior of zone-refined niobium and a lower purity grade. The zone-refined material was also obtained from the Materials Research Corp.; a typical analysis of this material is shown in Table I. The lower purity niobium was obtained from the Gallard-Schlesinger Chemical Corp., Carle Place, N. Y. This material was supplied in the form of cylindrical pellets ($^3/_{16}$ in. in diameter and $^3/_{16}$ in. long), assayed 99.5% Nb, and had an oxygen content of 300 ppm. Spectrographic analysis indicated Zr as the only major metallic contaminant.

In the case of tantalum both zone-refined and commercial grade were also used as starting materials. A typical analysis of the zone-refined material is shown in Table I. The commercial grade Ta assayed 98.8%, and, as determined spectrographically, contained Cr, B, Fe, Co, Al, Mo, and Nb as impurities. However, there was no significant difference in the behavior of the zone-refined and commercial grade metals.

Hydrogen was obtained from the Matheson Co., Gold Label grade, and assayed 99.99% H_2.

Procedure.—The high-pressure reactor, which served as the sample container, along with the auxiliary experimental equipment, has already been described in detail.[5] However, the procedure for synthesizing the hydrides differs substantially from that previously described and is given below.

The granular and pelletized materials were used in the as-received condition. The zone-refined rod material was cut into $^3/_8$-*in.* lengths. Samples were cleaned with acetone, weighed, and introduced into the high-pressure reactor which was then sealed. Initially, these operations were carried out in an argon-filled drybox, but such a precaution was found to be unnecessary and the samples were subsequently handled in air. Sample weights were ~6 g for V, ~10 g for Nb, and ~15 g for Ta. The reactor was attached to a pressure–vacuum manifold and the samples were outgassed while being heated to ~450°. At this point H_2 was introduced into the reactor until a pressure of 100 psia was attained. The sample was cooled over a period of ~1 hr to 350° and then again heated to 450° at which point the sample was outgassed until no evolution of gas was detectable. This procedure was repeated until the sample suddenly sorbed a large amount of hydrogen at which point it was considered activated. It was invariably more difficult to "activate" zone-refined material than the lower purity grades; apparently the presence of impurities serves to sensitize both V and Nb to hydrogen. After activation, the sample was outgassed once more at 450° and rapidly cooled to room temperature. At this point the sample was contacted with H_2 at ~950 psia. The sample usually reacted rapidly with the evolution of heat and a temperature rise of 25–50° was not uncommon. After several hours at room temperature the reactor was cooled and held at −78° overnight

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) For a recent general review see W. M. Mueller, J. P. Blackledge, and G. G. Libowitz, "Metal Hydrides," Academic Press, New York, N. Y., and London, 1968.

(3) (a) A. J. Maeland, T. R. P. Gibb, Jr., and D. P. Schumacher, *J. Amer. Chem. Soc.*, **83**, 3728 (1961); (b) G. Brauer and H. Muller, *Angew. Chem.*, **70**, 53 (1958); *J. Inorg. Nucl. Chem.*, **17**, 102 (1961).

(4) A. J. Maeland, *J. Phys. Chem.*, **68**, 2197 (1964).

(5) J. J. Reilly and R. H. Wiswall, *Inorg. Chem.*, **6**, 2220 (1967).

TABLE I
TYPICAL ANALYSIS OF ZONE-REFINED METAL

	Impurity content, ppm				Impurity content, ppm		
Impurity	Ta	V	Nb	Impurity	Ta	V	Nb
C	10	57	8	Mo	0.2	0.08	<0.7
H	<0.1	3	0.4	Na	0.015	<0.05	<0.03
N	2.3	3	4.0	Nb	25	0.8	
O	3.5	112	23.4	Ni	1.5	12.0	0.15
Ag	<0.004	<0.02	<0.3	Pb	0.08	<0.03	<0.02
Al	0.05	0.1	0.15	Pd	<0.08	15.0	<0.5
Bi	<0.04	<0.02	<0.007	Pt	<0.4	<0.04	0.02
Ca	<0.008	0.1	0.02	Rh	<0.002	<0.06	<0.06
Cd	<0.007	<0.03	<0.05	S	<0.02	0.1	0.07
Co	0.3	<0.15	<0.007	Si	0.2	0.1	0.6
Cr	0.2	<0.25	0.05	Sn	<0.006	<0.03	<0.3
Cu	0.02	<0.3	<0.01	Ti	0.01	6.0	<0.02
Fe	0.3	20.0	0.12	Ta		<0.3	100.0
Hf	<0.4	0.03	<0.02	V	0.01		<0.8
K	0.02	0.4	<0.04	W	1.2	7.0	6.4
Mg	0.006	<0.25	0.05	Zn	<0.004	<0.4	<0.015
Mn	0.01	<0.15	0.03	Zr	<0.1	<0.12	<0.3

while the H_2 pressure was maintained at ~950 psia. The reactor was then warmed to room temperature while continuing to maintain the H_2 pressure at ~950 psia. Then the hydride was decomposed by reducing the H_2 pressure to <1 atm and subsequently heating the sample to 450° under a dynamic vacuum. This procedure was repeated at least three times since it was found that such sorption–desorption cycles produced an extremely active material.

The procedure for obtaining the pressure–composition isotherms is essentially the same as that previously described in detail,[5] although the experimental temperatures are appreciably lower and the pressures higher. In brief, the procedure was as follows. The solid hydride phase was equilibrated with hydrogen until a hydrogen:metal atom ratio of 2 or greater was attained as indicated by the hydrogen take-up. The reactor was then heated to the required temperature by immersing it in a thermostatically controlled water bath. At temperatures above 80° the water bath was replaced by a similarly controlled electric furnace. At the specified temperature, H_2 gas was withdrawn from the reactor in small decrements by expanding the gas into a reservoir of known volume. The pressure and temperature of the gas in the reservoir were determined after each withdrawal. After each withdrawal, at least several hours was allowed for equilibrium to be reestablished in the reactor, and readings were taken when no detectable pressure change occurred over a period of 1 hr. The amount of hydrogen gas in the reactor assembly could be readily calculated at any time, since the pressure was continuously monitored with a transducer and the free volume was known; at experimental temperatures a correction factor was used to account for the transition in temperature between the reactor proper which was immersed in the heated zone and the upper portion of the reactor assembly which was at room temperature. When the dissociation pressure dropped to <0.5 atm, the water bath was removed and the reactor was heated slowly to 450° in order to decompose the monohydride. The evolved hydrogen was measured by venting it periodically into the calibrated reservoir. Finally, when the dissociation pressure dropped to ~20 mm, the reactor was cooled to room temperature, during which process it reabsorbed any hydrogen in the gas phase, and the hydrogen content of the solid residue was then determined using a conventional combustion train technique. Thus, the total hydrogen in the system was determined and the initial solid composition and its change as hydrogen was withdrawn could be readily calculated. Because of hysteresis effects, equilibrium was approached only from one direction, *i.e.*, by withdrawing hydrogen from the system.

Results and Discussion

A. Vanadium.—Previous work with the vanadium–hydrogen system has shown the existence of three crystalline phases.[4] At room temperature the phases consist of the original vanadium (α) phase in which hydrogen may dissolve to form a solid solution and which extends up to a composition corresponding to $VH_{0.05}$. Beyond $VH_{0.05}$ a new phase (β) appears and the composition region from $VH_{0.05}$ to $VH_{0.45}$ consists of a mixture of the α and β phases. From $VH_{0.45}$ to $VH_{\sim 0.9}$ only the pure β phase exists. Above $VH_{\sim 0.9}$ the dihydride (γ) phase appears which coexists with the β phase.

In Figure 1 are shown several pressure–composition isotherms of the V–H system in the region $VH_{0.8}$ to $VH_{2.0}$. The initiation of a pressure plateau at a composition approximating $VH_{0.95}$ marks the point at which the γ phase appears in the previously existing β phase. At ~40° the plateau extends from $VH_{0.95}$ to $VH_{2.00}$ at which point the isotherm rises sharply, marking the composition at which the β phase disappears and only the γ phase exists. As indicated in Figure 1, hydrogen may dissolve in the γ phase and H:V atomic ratios above 2.00 are possible. It will be noticed that the 67 and 78° isotherms cross one another in the single-phase (γ) region; this is a consequence of the nonstoichiometry of the system in which the higher temperature isotherm was obtained using a sample which had a greater initial hydrogen content (*i.e.*, $VH_{2.08}$ *vs.* $VH_{2.01}$ at room temperature). There is a slight slope in the plateaus shown in Figure 1. Libowitz[6] has shown that a thermal gradient across the sample could cause such an effect. In this case, however, we have ruled out this possibility since we have carried out many experiments using the same procedure and equipment with samples of similar geometry in which essentially flat plateaus were obtained (*e.g.*, see Figure 4). The phenomenon of a sloping plateau pressure is quite common in hydride systems and has been attributed in some cases to the presence of small amounts of impurities.[7] The reaction in the plateau region may be written as

$$1.92VH_{0.95} + H_2 \rightleftharpoons 1.92VH_{2.00} \qquad (1)$$

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(6) G. G. Libowitz, *J. Phys. Chem.*, **62**, 296 (1958).

(7) A. D. McQuillan, *Proc. Roy. Soc., Ser. A*, **204**, 309 (1950).

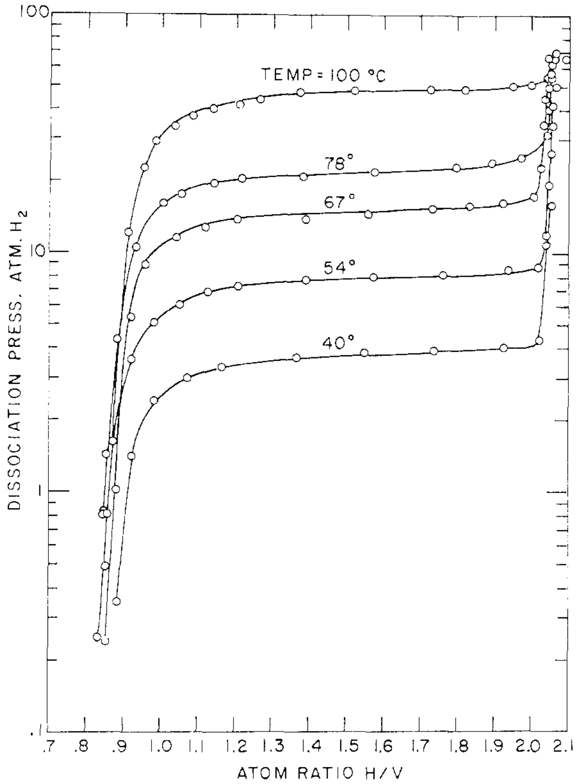

Figure 1.—Pressure–composition isotherms for the VH$_{\sim 1}$–VH$_{\sim 2}$ system.

A plot of the log of the dissociation pressure in the plateau region *vs.* the reciprocal of the absolute temperature yielded a straight line which obeyed the equation log $P_{\text{atm}} = (-2103/T) + 7.3416$. From these data the following thermodynamic quantities have been calculated for reaction 1: $\Delta H_{298} = -9.62 \pm 0.3$ kcal/mol of H_2, $\Delta F_{298} = +0.39 \pm 0.05$ kcal/mol of H_2, and $\Delta S_{298} = -33.6 \pm 1.0$ eu/mol of H_2.

Vanadium dihydride is unstable at room temperature but the decomposition in air is quite slow and material of a composition corresponding to $VH_{1.73}$ could be handled in air without significant hydrogen loss for short periods. Since $VH_{1.73}$ falls in the plateau region of the isotherms shown in Figure 1, it should be a mixture of the β and γ phases. This was confirmed by an X-ray diffraction pattern of the material which showed both the γ and β phases to be present. Upon elimination of the β lines the pattern was indexed and the γ phase was found to be cubic with a lattice parameter of 4.24 Å. This value is in fair agreement with previous work by Maeland, *et al.*,[3a] who, using material corresponding to $VH_{1.64}$, determined the γ phase to have an fcc structure with a = 4.271 Å. The $VH_{1.73}$ material had a gray metallic appearance and retained much of its original shape but with many cracks and fissures. It was very brittle and could be easily crushed to a powder.

Referring again to Figure 1, a sample of vanadium dihydride was decomposed until a composition of $VH_{0.88}$ was reached which should consist of the pure β-phase vanadium hydride since the steep isotherm in this composition region indicates the presence of only a single phase. Indeed, an X-ray diffraction pattern taken of this material showed only the presence of the β phase. The pattern was indexed and the $VH_{0.88}$ material was classified as having tetragonal symmetry with a = 3.02 Å and c = 3.33 Å. This is in good agreement with the results of Zanowick and Wallace,[8] who showed that in the pure β-phase region the lattice expands slightly as the hydrogen content is increased and material having a composition of $VH_{0.82}$ had a tetragonal structure with a = 3.00 Å and c = 3.31 Å. The $VH_{0.88}$ material was stable, did not react in air, and was similar in appearance to $VH_{1.73}$.

It is possible to use data abstracted from the pressure–composition isotherms to extend and clarify the hydrogen–vanadium phase diagram as shown in Figure 2.

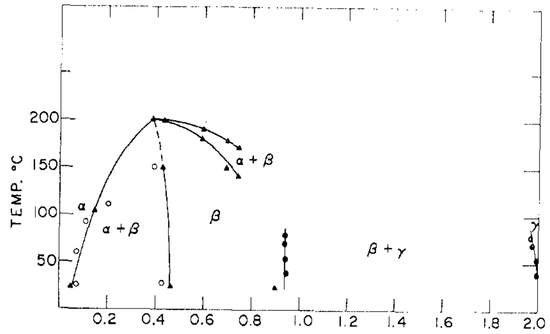

Figure 2.—Phase diagram of the vanadium–hydrogen system: ▲, A. J. Maeland, *J. Phys. Chem.*, **68**, 2197 (1964); ○, R. L. Zanowick and W. E. Wallace, *J. Chem. Phys.*, **36**, 2059 (1962); ●, this work.

In this diagram we have incorporated our results with those of Maeland[4] and with Zanowick and Wallace,[8] who explored the system between V and VH$_{\sim 0.9}$. We have drawn the $\beta/(\beta + \gamma)$ boundary at $VH_{0.95}$ but it should be noted that the transition of the isotherms from an almost vertical line to the horizontal plateau is relatively gradual over the interval $VH_{0.9}$–$VH_{1.0}$ and $VH_{0.95}$ is a compromise value. The shape of the various isotherms indicates that the boundary is not temperature dependent, at least up to 100°. The $(\beta + \gamma)/\gamma$ boundary on the extreme right side of the diagram can be determined more exactly as an examination of Figure 1 will show. At 40° this boundary is just about $VH_{2.00}$ and curves slightly to the left as the temperature is raised.

During the course of this work it was found that the dissociation pressure of the VH$_{\sim 1}$–VH$_{\sim 2}$ system was higher by a factor of >2 when the starting material was commercial grade vanadium instead of zone-refined vanadium. This effect, illustrated in Figure 3, is apparently due to the presence of impurities in the commercial grade metal. There was no difference, however, in the position of the phase boundaries in the system as determined from the isotherm shape. The reaction of H_2 with commercial grade vanadium is discussed in more detail elsewhere.[9]

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[8] R. L. Zanowick and W. E. Wallace, *J. Chem. Phys.*, **36**, 2059 (1962).

[9] Annual Report, BNL 50205 (S-72), Department of Applied Science, Brookhaven National Laboratory, Dec 31, 1969.

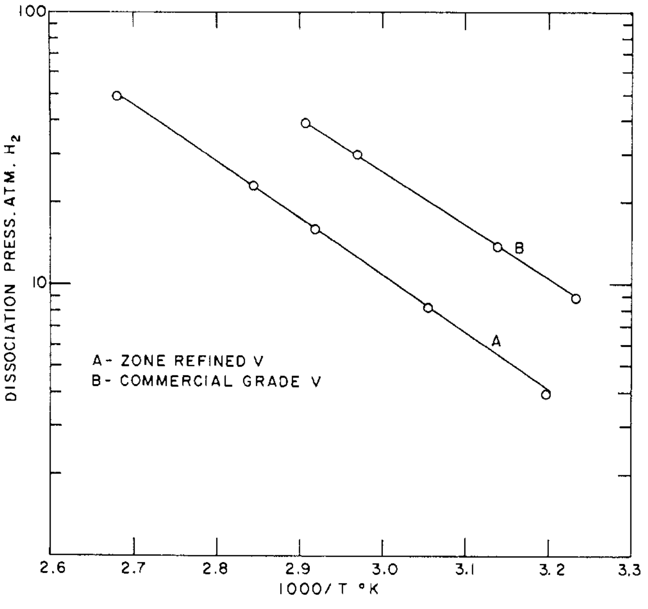

Figure 3.—The dissociation pressure of the $VH_{\sim1}$-$VH_{\sim2}$ system *vs.* 1000/T°K. The higher pressure obtained with commercial grade vanadium is attributed to the presence of impurities.

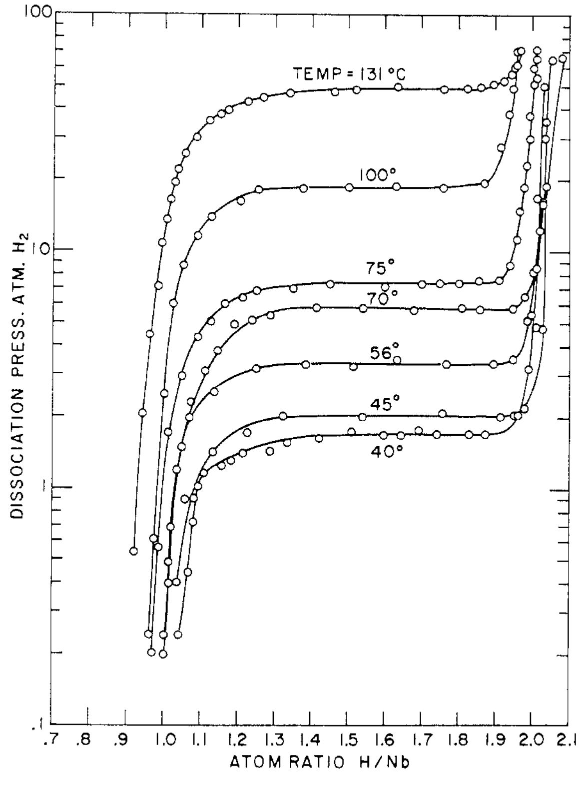

Figure 4.—Pressure–composition isotherms for the $NbH_{\sim1}$–$NbH_{\sim2}$ system.

B. Niobium.—The Nb–H_2 system behaves in a manner similar to the V–H_2 system. In Figure 4 are shown a number of pressure–composition isotherms for the region extending from $NbH_{\sim0.9}$ to $NbH_{\sim2.0}$. The isotherms rise steeply on the left until a composition of $NbH_{\sim1.1}$ is reached where the γ-dihydride phase appears. At 40° the $\gamma + \beta$ mixed-phase region extends to $NbH_{\sim1.9}$ where the isotherm begins a steep ascent indicating the disappearance of the β phase. It may be noted that the lower temperature isotherms indicate an appreciable solubility of hydrogen in the pure γ phase which resulted in hydrogen contents up to a composition corresponding to $NbH_{2.081}$, not a surprising result since Brauer and Muller[3b] obtained $NbH_{2.07}$ *via* the electrolytic method, and that niobium dihydride, as are other group Va hydrides, is a nonstoichiometric compound. Here, too, it is possible for the isotherms to cross one another in the single-phase (γ) region because of the variable initial hydrogen content.

The reaction for the plateau region may be written as

$$2.5NbH_{1.1} + H_2 \rightleftharpoons 2.5NbH_{1.90} \qquad (2)$$

A plot of the log of the dissociation pressure *vs.* the reciprocal of the absolute temperature yields a straight line obeying the equation $\log P_{\mathrm{atm}} = (-2090/T) + 6.8662$. From these data the following thermodynamic quantities were calculated for reaction 2: $\Delta H_{298} = -9.56 \pm 0.3$ kcal/mol of H_2, $\Delta F_{298} = -0.21 \pm 0.05$ kcal/mol of H_2, and $\Delta S_{298} = -31.4 \pm 1.0$ eu/mol of H_2.

Niobium dihydride has a gray, metallic appearance, is not pyrophoric, and appears to be quite stable in air. Most of the individual pellets of the sample examined had retained their original shape, although all exhibited many cracks and fissures. The material was very brittle and could easily be ground into a fine powder. The density of niobium dihydride ($NbH_{1.96}$) was 6.7 g/cm^3 as measured under benzene using a pycnometer. An X-ray diffraction pattern was taken of a product whose composition was determined to be $NbH_{1.98}$. The pattern was indexed and dihydride was found to have cubic symmetry with a = 4.53 Å, a value in excellent agreement with that of Brauer and Muller,[3b] who reported the niobium dihydride as having a face-centered cubic structure with a = 4.536 Å.

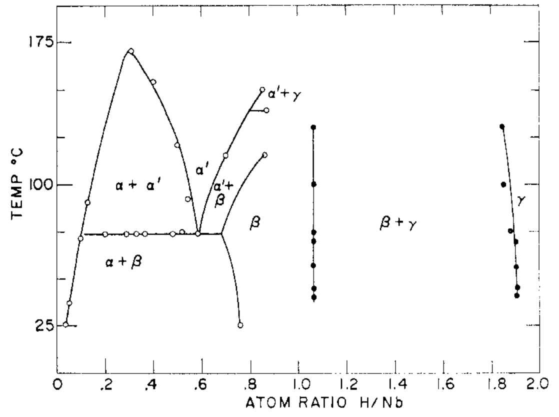

Figure 5.—Phase diagram for the niobium–hydrogen system: ○, R. J. Walter and W. T. Chandler, *Trans. AIME*, **233,** 762 (1965); ●, this work.

A sample of niobium dihydride was decomposed to give a product having the composition $Nb_{0.96}$. An examination of Figure 4 will show that a material of this composition should consist only of the β phase. This conclusion was supported by evidence obtained from an X-ray diffraction pattern taken of $NbH_{0.96}$

which showed only the presence of the β phase. The pattern was indexed and indicated the material had a distorted cubic symmetry with $a = 3.44$ Å. Komjathy[10] reported $NbH_{0.82}$ to have a distorted bcc structure with $a = 3.409$ Å. The degree of distortion is small and Wainwright, *et al.*,[11] calculated a c/a ratio of 1.005 for $NbH_{0.85}$.

As with vanadium it is possible to construct a phase diagram of the niobium–hydrogen system from data abstracted from the pressure–composition isotherms. In Figure 5 such a diagram is shown in which our results have been combined with those of Walter and Chandler,[12] who have constructed a phase diagram for the Nb–H system up to $NbH_{0.86}$. It is somewhat difficult to place exactly the $\beta/(\beta + \gamma)$ phase boundary as determined by the isotherm shape; however, its placement at $NbH_{1.1}$ is consistent with recent results obtained by Aronson, *et al.*,[13] in magnetic susceptibility studies. The $(\beta + \gamma)/\gamma$ boundary can be more readily defined and is approximately at $NbH_{1.95}$ at 40° but is displaced toward the left as the temperature is increased.

Acknowledgments.—The authors wish to thank Mr. Jonathan Hughes and Mr. Albert Holtz for their expert assistance in the laboratory.

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[13] S. Aronson, J. J. Reilly, and R. H. Wiswall, *J. Less-Common Metals*, in press.

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Preparation and Properties of Some Fluorocarbon Derivatives of Tin

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The Mössbauer spectra of the compounds $(CH_3)_3SnR_f$ show a quadrupole splitting which is believed to be due to an electronegativity difference between the methyl groups and the R_f group. The magnitude of the splitting indicates that the electronegativity of the R_f group increases in the order: $CH_2F < CHF_2 < CF{=}CF_2 < CF_3 \approx CH(CF_3)_2 < CF_2CF_3 < C{\equiv}CCF_3 < CF(CF_3)_2$. The compound $(CH_3)_3SnCF_2H$ wasp repared by treating $(CH_3)_3SnH$ with $(CH_3)_3SnCF_3$. Apart from $(CH_3)_3SnCF_3$ none of the compounds appears to be a useful carbene source.

Introduction

Trimethyltrifluoromethyltin, $(CH_3)_3SnCF_3$, was first prepared by the reaction of trifluoroiodomethane with hexamethylditin[1–3] (eq 1, $R_f = CF_3$). Clark and

$$(CH_3)_3Sn{-}Sn(CH_3)_3 + R_fI \xrightarrow[h\nu]{} (CH_3)_3SnR_f + ISn(CH_3)_3 \quad (1)$$

Willis[1] found that it was a good source of difluorocarbene (eq 2) on pyrolysis at 150°. The carbene produced in this way has been added to C═C bonds to

$$(CH_3)_3SnCF_3 \xrightarrow{150^\circ} (CH_3)_3SnF + CF_2 \quad (2)$$

yield cyclopropanes[1,4,5] and to C≡C bonds to yield cyclopropenes.[4–6] The addition to *cis*- and *trans*-butene occurs stereospecifically indicating that the carbene is produced in the singlet state.[7] This is the usual state of difluorocarbene from other sources.[8]

Seyferth and his coworkers[9] have recently used the same tin compound as a source of difluorocarbene at lower temperatures in DME solution by the method indicated in eq 3. Here also the carbene adds to olefins

$$\begin{gathered}(CH_3)_3SnCF_3 + I^- \longrightarrow (CH_3)_3SnI + CF_3^- \\ CF_3^- \longrightarrow F^- + CF_2\end{gathered} \quad (3)$$

to give cyclopropanes.[9] Very little is known about the abilities of other fluorocarbon derivatives of tin to act as sources of carbenes so it was decided to synthesize a few to investigate their thermal decomposition.

Recently there have appeared some reports that the Mössbauer spectra of compounds of the type R_3SnR' show splittings which appear to be caused, at least in the main, by differences in σ bonding, that is, electronegativity differences between R and R'.[10–12] Parish and Platt[11] reported a quadrupole splitting for $(CH_3)_3SnCF_3$ ($\Delta = 1.38$ mm/sec) and slightly smaller but well-resolved splittings for R_3SnR' ($R = CH_3$ or C_6H_5; $R' = C_6F_5$ or C_6Cl_5). The splitting in the $R_3SnC_6F_5$ compounds is probably due to electronegativity differences since nmr studies indicate little π donation from the C_6F_5 group to $(CH_3)_3Sn$.[13] Thus the investigation of the Mössbauer absorption spectra of the fluoroalkyl-

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