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HYDRIDES AND METAL-HYDROGEN SYSTEMS

Final Report to NEPA Division

By
Thomas R. P. Gibb, Jr.

AEC RESEARCH AND DEVELOPMENT REPORT

April 30, 1951

Metal Hydrides Incorporated

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Foreword and Acknowledgments

This report includes reference to all significant phases of a research and development contract carried out under the sponsorship of the NEPA Project. Certain aspects of the program have been carried out in considerable detail; other phases have been covered in a somewhat cursory way depending on the current requirements of the sponsor. Work under the contract was commenced on August 17, 1948, and terminated on April 30, 1951.

It is a pleasure to acknowledge the full cooperation of the Chemistry Section of the NEPA Project, especially Dr. V. P. Calkins, Dr. K. Anderson, Mr. J. W. Johnson, Mr. J. J. Neely, and also of Drs. A. J. Miller, Robert Echols, and William Ergen, of the Physics Section.

The work reported here was carried out under the supervision of Thomas R. P. Gibb, Jr., and (since November 16, 1949) of M. Douglas Banus. All members of Metal Hydrides Incorporated research staff participated in each phase; however, principal credits are as follows:

M. Douglas Banus	Iron and nickel hydrides. Melting of lithium borohydride. Synthesis and properties of quaternary compounds.
Robert W. Bragdon	Preparation of pure titanium hydride. Synthesis and properties of quaternary compounds. Thermodynamic calculations. Tungsten and thorium borohydride studies.
Alfred A. Hinckley	Aluminum hydride studies. Preparation of pure saline hydrides.
Charles H. Lewis	Compaction of titanium hydride. Lithium borohydride preparation.
Henry W. Kruschwitz, Jr.	Low-pressure U-H studies. Density determinations. Calculations and graphs.
James J. McSharry	High-pressure dissociation studies of Ti, U, Ca, Sr, Ba, Li, Na hydride systems. Diffusion studies.
William H. Pasfield	Preparation and pyrophoricity of UH_3 . Compaction of UH_3 .
Harry O. Warren	Preparation of nitrides.
F. H. Wilson	Hydrogen diffusion (early work).

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In addition acknowledgment is made of consulting work and assistance by the following:

Daniel P. Cushing Consultant	Metallographic studies.
Howard T. Evans M.I.T.	X-ray diffraction studies of TiH_2 .
General Chemical Co.	Loan of a cylinder of tungsten hexafluoride gas.
Gurnard Manufacturing Co.	Fabrication of stainless steel bombs, etc.
Eugene V. Mingotti Middlesex Welding Co.	Development of welded closures.
Edward Washken Washken Laboratory	X-ray diffraction studies of alleged iron and nickel hydrides.
Harold A. Brown Metal Hydrides Inc.	Large-scale preparation of titanium hydride.

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Summary

The work reported herein deals with the preparation and physical properties, especially thermal dissociation pressures, and densities of hydrides, hydrogen-metal systems, and mixtures of hydrides with other substances. Possible applications as moderators, high-temperature neutron shields and low-temperature shields are cited and design problems discussed. Most of the data on dissociation pressures cover ranges and compounds not hitherto explored because of experimental difficulties and the basic knowledge of the thermal behavior of hydrides has been substantially increased. New hydrides have been prepared and several reported in the literature have been shown not to exist.

The following compounds, mixtures, and systems have been studied: Ti-H, U-H, Li-H, Na-H, Ca-H, Ba-H, Th-H, Sr-H; NaH-NaF, NaH-NaOH, NaH-CaH₂, LiH-LiF, CaH₂-CaF₂, CaH₂-CaC₂, CaH₂-Ca₃N₂; FeH₃ (alleged), NiH₂ (alleged), Ti(BH₄)₃, Th(BH₄)₄, WH₄ (attempted), W(BH₄)₄ (attempted), AlH₃, LiBH₄, (CH₃)₄NBH₄, (CH₃CH₂)₄NBH₄, and (CH₃)₃BzNBH₄.

Among the hydrides are compounds having an N_H comparable to water yet stable at red heat, compounds giving a neutron shield weight less than half that of water, and compounds suitable for use as high-temperature moderators containing large amounts of hydrogen.

Recommendations are made for further studies.

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Introduction

Hydrides are of considerable significance in the design of nuclear energy sources by virtue of the unique ability of hydrogen to slow down fast neutrons. Use of hydrides in moderators and neutron shields is considered because respective compounds of this family have (a) the highest hydrogen content per unit volume (b) the highest hydrogen content per unit weight and (c) a higher thermal stability at elevated temperature than other hydrogenous materials of comparable hydrogen content. Thus the density of hydrogen in a number of hydrides is considerably greater than the density of solid hydrogen at its freezing point. Furthermore for shielding purposes a heavy metal such as uranium, thorium, hafnium, tantalum, or barium, etc. may be combined with hydrogen to form a hydride having high gamma absorption as well as neutron attenuation.

While comprehensive studies of hydride stability toward radiation are not available, the reversibility of thermal dissociation of most binary hydrides shows recombination to be extremely rapid and complete. This would render stability to radiation most probable for such hydrides.

Prior to the work undertaken in this laboratory, comparatively little was known about hydrides, and many chemists and physicists were completely unaware even of the existence of such compounds. Indeed they have been referred to as "esoteric materials." The literature contains a relatively small body of information which, incidentally, has been compiled by this laboratory and published⁽¹⁾. Unfortunately little of these early data is pertinent to NEPA's purposes and still less of it may be considered reliable. Thus reported dissociation pressures may vary by orders of magnitude from one author to another and even the formulas assigned to hydrides vary widely.

One noteworthy characteristic of most early work is a general failure to take into account the relation between dissociation pressure and composition. Many workers evidently believed that the dissociation of hydrides was comparable to that of, say, carbonates, where equilibrium pressure is independent of the extent of dissociation. (This impression is confirmed by recent and reliable studies of the exceptional uranium-hydrogen system⁽²⁾, where equilibrium pressures are indeed independent of composition over a wide range but only at relatively low temperature.) Since the thermal stability of hydrides is, of course, a function of dissociation pressure, the principal emphasis of the work in this laboratory has been placed on measurement of the latter. Rather than discuss the history of hydride development here, reference may be made to the above-cited bibliography and to NEPA 669-IHR-13, 546-IHR-C9, 629-IHR-C11, and 790-SCR-26.

From the foregoing it follows that one of the principal reasons for undertaking the present study was to provide reliable and extensive data on the nature and properties of hydrides, particularly dissociation pressure, composition, and density. As will be seen from the bulk of

- (1) "A Bibliography on the Hydrides of Metals and Metalloids," Metal Hydrides Incorporated, Beverly, Mass., 2nd Ed., December, 1950.
- (2) CC 1201.

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data contained herein, this objective has been reached, although as in most research programs, each new discovery reveals the promise of still further developments.

One of the first objectives of the NEPA program was the construction of rectangular briquets of hydride able to withstand bright red heat in contact with air for construction of a neutron shield. It was soon evident that any hydride or hydrogenous material of high-hydrogen content would have to be contained for this purpose in an impervious shell capable of withstanding considerable pressure. It thus became necessary not only to ascertain the magnitude of this pressure, but also to determine the hydrogen permeability of suitable container materials. These two phases of the program were carried out and the required design data and method of fabrication outlined in a Topical Report⁽³⁾. During the course of this work, the titanium-hydrogen system was chosen as a typical metal-hydrogen system and was fully investigated⁽⁴⁾. The uranium-hydrogen system was chosen as an atypical system and likewise investigated⁽⁵⁾.

The need for a hydride of a very heavy metal for combined neutron and gamma shielding was realized and to some extent prompted the selection of uranium hydride for investigation. This need also initiated a research program on tungsten hydride which had never been prepared. Work was continued to the point where evidence was obtained that tungsten hydride would probably not be suitable for NEPA purposes and the program was terminated. This work entailed preparation and study of aluminum hydride,⁽⁶⁾ titanium borohydride, thorium borohydride, and attempted preparation of tungsten aluminohydride and tungsten borohydride.⁽⁷⁾ Because of a modification of shield design and as a result of certain calculations⁽⁸⁾, it became necessary to consider hydrides of low density for use in a peripheral shield operating at relatively low temperatures. The criteria of suitability are (1) maximum radiation stability (2) minimum shield weight compared to water (measured by maximum ratio of water shield weight/hydride shield weight). In addition it has been required that the material be non-hazardous (in the event of puncture) and suitable for use as an auxiliary jet fuel. Although no radiation stability measurements have yet been made by or for this laboratory, it seems likely from analogous cases that an ionic compound, i.e., a salt will show greater stability than a covalent compound having a comparable heat of formation. This laboratory accordingly has prepared a number of light saline hydrides and studied their thermal stability. Aqueous and other solutions of some of these have also been considered with added heavy metals, containers, casting in molds, etc.

- ✓ (3) Topical Report No. 5, "PCT Relations Applicable to Hydrides in Rigid Containers," October 12, 1950.
- ✓ (4) Topical Report No. 1, "The Titanium-Hydrogen System," February 17, 1950.
- ✓ (5) Topical Report No. 6, "Uranium Hydride and the Uranium-Hydrogen System," March 21, 1951.
- (6) Topical Report No. 7, "The Reactions of Borohydrides and Alumino-hydrides with Wolfram (VI) Halides," November 8, 1950.
- (7) Topical Report No. 4, "Aluminum Hydride Etherate," November 20, 1950.
- (8) Topical Report No. 2, "Shield Weight Calculations," March 6, 1950.

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Several months prior to termination (November, 1950) at the request of NEPA, a third objective was set up, viz., development of molten hydride systems in which a nuclear fuel could be dissolved. This was subsequently modified to include hydride systems relatively stable in the solid state up to 1000° C for use as moderators. This objective was given top priority during the last few months of the contract, and a large number of systems was investigated. Thus the work reported herein was carried out in three major programs: (1) high-temperature shielding materials of high N_H (2) low-temperature shielding materials of high-hydrogen content and (3) thermostable materials for use as moderators. These programs are more or less separate and distinct, since the requirements to be met under each category are different. In addition to these major programs, a considerable number of minor projects were undertaken, e.g., the above-mentioned studies of container materials, container fabrication, and hydrogen permeability, preparation of intermediates, a study of reaction mechanism, preparation and purification of raw materials, methods of analysis, etc.

The work reported herein has resulted in the following accomplishments:

- (1) A new understanding of the nature of hydrides.
- (2) Extension of thermal dissociation data on many hydrides to high-temperature regions never studied hitherto.
- (3) Measurement for the first time of the thermal dissociation of several stoichiometric hydrides and of the relation of hydrogen content to equilibrium pressure.
- (4) Determination of the effect of a number of added substances on dissociation pressure and density of hydrides.
- (5) Preparation and characterization of novel hydrides, together with refutation of a number of previously claimed compounds.
- (6) Measurement of hydrogen permeability of welded containers, the development of fabrication and handling techniques, and a quantitative study of "model" containers.

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Part I

Metallic and Heavy-Metal Hydrides as Shielding Materials

Contents: Titanium Hydride, Uranium Hydride, Thorium Borohydride, Tungsten Hydride and related compounds, Container Design

I-1 Titanium Hydride(4)

This hydride was selected as a reference substance and also because no reliable data were available in the literature. It also contains the maximum number of hydrogen atoms per cubic centimeter ($N_H = 9.11$) of all known metallic hydrides (i.e., alloy-type hydrides). The density of hydrogen in titanium "solution" at 25°C is nearly two times greater than the density of solid hydrogen at its melting point (0.16 g./c.c. vs. 0.076 g./c.c.). To compress gaseous hydrogen to the volume it occupies as titanium hydride would require pressures well above the range of feasibility, since one volume of hydride at room temperature contains about 1700 volumes of hydrogen.

I-1-1 Dissociation Pressure

The equilibrium pressures of hydrogen over titanium-hydrogen solid phase were determined by heating a stainless steel bomb containing the hydride and some excess hydrogen. When the pressure just begins to exceed that due to thermal expansion, the temperature and pressure are taken as representing an equilibrium over stoichiometric TiH_2 . On heating to higher temperatures, additional dissociation takes place and the pressures observed are, therefore, those in equilibrium with a solid phase containing less than stoichiometric amounts of hydrogen. From the known volume and pressure of the system, the amount of hydrogen dissociated from the solid phase is found and subtracted from that originally present to give the composition of the solid phase. The results of this study are shown in Figs. (1) and (2). The notation "%" refers to the per cent of maximum (stoichiometric) hydrogen present in the solid phase; thus TiH_2 has a composition of 100% and TiH a composition of 50%. The profound effect of a minute removal of hydrogen is clearly indicated in both figures, although this effect is not emphasized by the logarithmic ordinate (necessary because of the hundred-thousandfold range of pressures covered). For purposes of convenience the dissociation pressure of 99% and 96% and 70% hydrides are given in Table I.

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The dissociation of titanium hydride is completely and rapidly reversible except at very low pressures in the region of 600° C as shown in Fig. (3). Data for the latter figure were obtained by a conventional technique reported elsewhere⁽⁴⁾. The complex hysteresis loop shown in the 600° isotherm may have a minor bearing on radiation stability inasmuch as it indicates that hydrogen once in the lattice tends to be slightly more reluctant to leave than expected. No hysteresis or departure from equilibrium has been observed under any other conditions except when impurities were introduced. Indeed partially hydrided titanium absorbs hydrogen very rapidly and exothermically at room temperature. The relation of temperature, pressure, and composition is shown in Fig. (3a) where n is the number of H atoms per atom of Ti.

I-1-2 Effect of Impurities

The rate of attainment of equilibrium and the composition at equilibrium are very dependent on the purity of the metal and of the gas used. Presence of traces of air inhibit hydriding and lower the attainable content of hydrogen. Moreover the equilibrium pressure is substantially higher over a contaminated system than over a pure system of the same hydrogen content. This is of considerable importance in the design of hydride-filled containers and as a precaution it is recommended that such containers be equilibrated prior to use. One significant observation is that traces of nitrogen are beneficial in systems containing less than 90% theoretical hydrogen at pressures near one atmosphere. Contamination of the previously formed "hydride (60-90%) by 0.1% nitrogen increased the equilibrium hydrogen content by a considerable (but variable) percentage; however, nitrogen- (and possibly oxygen-) contaminated specimens could not absorb over about 95% of the theoretical amount of hydrogen. It was hoped that some further work could be done on ternary systems of titanium with nitrogen, nickel, magnesium, etc. and hydrogen, but this was not commenced. A single observation was made, however, that a zirconium-nickel alloy retained much more hydrogen than pure zirconium at room temperature.

I-1-3 Thermodynamic Properties

The thermodynamic properties of the titanium-hydrogen system were calculated to be as follows:

Table II

For Reaction $\text{TiH}_2 \rightarrow \text{TiH}_2\text{-dH}^*$
(T is in °K unless otherwise stated.)

Heat of Dissociation	25° C	$\Delta H = + 5168 \text{ cal/mol H}_2$
Heat of Dissociation	-273° C (0° K)	$\Delta H_0 = + 4870 \text{ cal/mol H}_2$
Free Energy of Dissociation	25° C	$\Delta F_0 = + 709$
	$p = 1 \text{ atm.}$	
Free Energy of Dissociation		$\Delta F = 4870 - 2.3 T \log_{10} T - 8.27T$
Entropy of Dissociation	25° C	$\Delta S = 14.96 \text{ e.u.}$
Temperature at which $\Delta F = 0$		$T = 73^\circ \text{ C}$
Dissociation Constant (atm.)		$\log_{10} K_p = \frac{4870 - 2.3 T \log_{10} T - 8.27 T}{-4.58 T}$

* dH represents an infinitesimally small quantity of hydrogen.

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Table II

For Reaction $\text{TiH}_{1.93} \rightarrow \text{TiH}_{1.93-dH}^*$

Heat of Dissociation	25° C	$\Delta H = + 19,150 \text{ cal/mol H}_2$
Heat of Dissociation	-273° C	$\Delta H_0 = + 18,850 \text{ cal/mol H}_2$
Free Energy of Dissociation	25° C	$\Delta F_0 = +10,030$
	p = 1 atm.	
Free Energy of Dissociation		$\Delta F = 18,850 - 2.3 T \log_{10} T - 23.9 T$
Entropy of Dissociation	(25° C)	$\Delta S = 32.3 \text{ e.u.}$
Temperature at which $\Delta F = 0$		$T = 1480^\circ \text{ C}$
Dissociation Constant (atm.)	$\log_{10} K_p =$	$\frac{18,850 - 2.3 T \log_{10} T - 23.9 T}{-4.58 T}$

* dH represents an infinitesimally small quantity of hydrogen.

An equation was also devised which expresses the relation of equilibrium pressure to temperature and composition (% H) in the ascending portions of the isotherms of Fig. (2) in the regions above approximately 80% composition:

$$\log P_{cm} = 3.75 \log C + 0.00765 T - 7.70$$

Here T is in degrees Kelvin and the composition term C is $\% / (100 - \%)$, where % refers to per cent of maximum hydrogen content. Note that this is equivalent to $n / (2 - n)$, where n is the number of H atoms per Ti atom.

I-1-4 X-Ray Diffraction and Density

A cursory x-ray diffraction study of the Ti-H system confirms the phase relationships implied by the plateaus of Fig. (2). It also reveals that the limiting high-temperature phase TiH_2 is novel and metastable at room temperature, reverting to the familiar beta phase⁽⁹⁾ in a day or two; characteristic diffraction lines at $d = 2.076$ and $1.801 \text{ \AA}$. The density of the beta TiH_2 by x-ray measurement is 3.96 g./c.c. at 25° C . A linear relation exists between H-content and density (measured by helium displacement)⁽¹⁰⁾ contrary to the conclusion of Biltz⁽¹¹⁾. This relation is:

$$d_{25} = 4.41 - 0.325 n$$

where n is the number of H atoms per Ti atom. The density of stoichiometric TiH_2 is 3.75 g./c.c. at 25° C by helium displacement, and this figure is regarded as more reliable than the higher x-ray value cited because of the evident presence of two phases.

(9) Hagg, G., Z. phys. Chem. B11, 433-454 (1931).

(10) Schumb, W. C. and Rittner, E. S., J. Am. Chem. Soc. 65, 1692 (1943).

(11) Biltz, W., "Raumchemie der festen Stoffe," L. Voss, Leipsig, 1934.

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The compactibility of titanium hydride powder was determined and methods developed for the preparation of dense, fairly durable discs having a density of 3.24 g./c.c. (86.5% of theoretical). The -324 mesh powder was lubricated with 4% camphor (dissolved in carbon tetrachloride as nearly saturated solution) and pressed in a 1.830" diameter die (Uniloy) at 200-300 tons force (or 110 T.S.I.). The pellets have an initial density of 3.24 g./c.c., but after vacuum removal of the camphor at 100° C, the pellets expand slightly. By using 1% camphor and pressing at 225 T.S.I., a density of 85% of theory is attained for delubricated pellets. (See Fig. (3) Topical Report No. 5 for a plot of d ratio vs. pressure.) No substantial increase in density is observed between 100 and 225 T.S.I. The pellets cannot be ignited by a match or bunsen flame applied to one edge.

I-1-5 Containers for the Ti-H System

It is evident from the foregoing that on the basis of hydrogen content, titanium hydride is an excellent material for shielding purposes at elevated temperatures. The necessity for a container is obvious, and it is of interest to set up a model container in order to calculate the optimum hydrogen content per unit total volume of hydride plus container. This type of calculation must be made for any reversibly dissociating hydride. The complexity of the calculation is not great, but it includes points which might easily be overlooked.

A model container was set up by selecting a material of construction having a tensile strength of 50,000 psi up to 800° C and impervious to hydrogen. This is formed into a cylinder whose length is ten times its diameter and filled with compressed, powdered hydride having a theoretical density (density variation with composition is corrected for). The maximum safe working pressure of a welded-end cylinder is calculable via the ASME code formula (see section I-4). One may then calculate the relation between the required wall thickness or container bulk and the hydrogen content of the hydride at a series of temperatures. Since the dissociation pressure is higher for higher compositions, the wall thickness must be increased to withstand the higher pressure. Thus there must be an optimum point where the hydrogen content and wall thickness are such that the overall N_H of the unit is at a maximum. The result of such calculations is shown in Fig. (4), where N_H' represents the average number of H atoms per c.c. of the whole unit.

It is readily seen that under the postulated restrictions, the maximum attainable N_H' of the hydride-filled cylinder is somewhat less than the N_H of pure TiH_2 , and that N_H' decreases rapidly with increasing temperature. The effect of diffusion loss may be made insignificant by using a sufficiently large container so that the walls are several millimeters thick or by using an impervious material such as molybdenum. (See Fig. 12, Topical Report No. 5 and also section I-4 of this report.) A loss of 0.01g c.c. hydrogen per cm.² area per hour per millimeter thickness has been achieved with 347 alloy stainless steel under 76 cm. hydrogen pressure and 650° C. A calculated hydrogen loss from a molybdenum cylinder amounts only to the order of 10⁻⁹ g. of hydrogen per hundred hours under the restrictions of container bulk cited above and

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at 800° C, $P = 10^4$ cm. (The diameter of this cylinder is 20 cm.) (See Topical Report No. 5, Table IV for further details.) If it is assumed that a density of 85% theoretical may be achieved by compressing TiH_2 , then the N_H' of the units is given in Table III.

Table III

Maximum N_H' of Contained TiH_2

$T^\circ C$	N_H'
500° C	7.4
650° C	7.1
800° C	6.5

A description of the hydrogen concentration gradient in a container whose ends are at different temperatures was worked out and cited in Report No. 5 (p 17). This report contains details of the experimental work and calculations cited above.

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I-2 Uranium Hydride

The uranium-hydrogen system has been studied previously only over a very narrow range⁽¹²⁾. This system is not typical and still presents a number of problems. The work of this laboratory, however, has brought about a fuller understanding of uranium hydride by extension of dissociation data to high-pressure and temperature regions. Means of handling and compacting the finely divided solid have been developed and ways have been found for reducing its hazardous pyrophoric character. Uranium hydride, UH_3 , contains considerably less hydrogen per c.c. than titanium hydride and is less stable thermally. Its density is much greater (10.5 g./c.c.) and the stopping power for gamma radiation is therefore superior. This factor governed choice of the material for study.

I-2-1 Dissociation Pressure

The equilibrium pressure was studied by the techniques developed in the work on TiH_2 . Earlier work was confirmed and greatly extended. Contrary to the impression given by earlier work, however, the dissociation pressure was found to depend on hydrogen content in much the same way as in the case of the Ti-H system. The dissociation curves are shown in Figs. (5), (6), and (7). The latter figure indicates the agreement with the single curve given in the cited reference. It will be noted that our data in Fig. (7) (J.J.M.) are for stoichiometric UH_3 , whereas the earlier data are for an unspecified composition in the vicinity of $UH_{2.88}$ or 96%. The quantitative relation of dissociation pressure to hydrogen content is clearly shown in Figs. (5) and (6), where "%" refers to per cent of maximum theoretical hydrogen content or $100 n/3$, where n is the number of H atoms per uranium atom. The three-dimensional sketch shown in Fig. (8) expresses the relation between n , pressure, and temperature. For convenience the actual dissociation pressure over UH_3 and 96% material is shown in Table IV.

Table IV

Selected Values of Dissociation Pressure over U-H System

UH_3		$UH_{1.92}$	
$T^{\circ}C$	P_{cm}	$T^{\circ}C$	P_{cm}
524	771	630	832
397	298	560	198

(12) Newton, A. S., Warf, J. C., Butler, T. A., and Spedding, F. H., Nucleonics Δ , (1949) (series of articles).

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The reversibility or rate of attainment of equilibrium in the U-H system is less pronounced than for the Ti-H system. Equilibrium may require days instead of minutes at low temperature. At high temperature it is attained more rapidly, i.e., in one-half hour, but the rate of absorption is variable. This slowness of recombination is of importance in predicting radiation stability; however, in a high-energy flux, recombination may prove to be rapid.

Pronounced hysteresis of an unusual form was noted for uranium hydride containing 20-90% stoichiometric hydrogen at 400° C, where the pressure is below one atmosphere; however, at higher compositions and pressures, it was not of sufficient magnitude to be observed. The phenomenon of high-pressure development by rapid alternate heatings and coolings was not studied, but the rate of attainment of equilibrium at 600° C under several atmospheres' pressure is sufficiently rapid so that it appears unlikely that such "pressure pumping" would be observed.

I-2-2 Purity and The Effect of Impurities

Qualitatively the U-H system appears less susceptible to impurities than the Ti-H system. Mallinckrodt AR grade uranium, which contains up to 2% oxygen (or 18% U₃O₈), gives a hydride having a U/H ratio of 1/2.6 in fair agreement with the metallic uranium content; thus oxygen does not appear as serious an inhibitor as in the case of titanium. The effect of nitrogen was not investigated, nor was any study made of the rate of hydrogen absorption in view of the excellent study by Burke and Smith⁽¹²⁾ (also Gueron and Yaffe⁽¹³⁾). The material made in this laboratory corresponds to the formula UH_{2.094}. There is some evidence, however, that traces of hydrogen are easily lost on brief evacuation at room temperature or by contact with air. The particles are small and brittle. Under the microscope the sizes range from 1.5 microns to 50 microns with the mode at 15 microns. Particles resemble coke in appearance with occasional thin spikes protruding. Material prepared at 800 psi was very similar to that prepared at atmospheric pressure.

I-2-3 Thermodynamic Properties

From the slopes of Fig. (5), the differential heats of dissociation may be calculated and thence other thermodynamic constants as follows:

Table V

Thermodynamic Properties of the U-H System

$\Delta H = 7935$ cal/mol
$\Delta H_0 = 5559$ cal/mol
$\Delta H_{298} = 6542$ cal/mol
$\Delta F_{298}^0 = 2093$ cal/mol
$\Delta S_{298} = 14.93$ e.u.

(12) Burke, J. E. and Smith, C. S., J. Am. Chem. Soc. 69, 2500 (1947).

(13) Gueron, J. and Yaffe, L., Nature 160, 575 (1947).

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These values are for stoichiometric UH_3 and pertain only to this composition.

An equation relating hydrogen content (C) to dissociation pressure (P) and absolute temperature T is given as:

$$\log P_{\text{cm}} = 0.735 \log C + 0.00640 T - 3.25$$

where $C = \%(100-\%) = n/(3-n)$.

This equation is applicable between the region defined by $\log P > 3$ and the line defined by:

$$\log P_{\text{cm}} = 4.64 - 0.5135 \log (n/(100-n))$$

This latter equation represents the state of the system when the limiting phase (close to UH_3) starts to form. The region of applicability is thus the broad sloping plane of Fig. (8). The dissociation pressure is evidently almost independent of composition outside of this region.

I-2-4 Density and Compaction

Because of the considerable difficulty of precise measurements and in view of earlier work⁽¹⁴⁾, the density was not determined except for one check point which was measured to confirm the reported relation of density to hydrogen content. Agreement with (14) was excellent. A curve of density vs. hydrogen content is given as Fig. (9) of Topical Report No. 6. This relationship is nearly linear for compositions represented by UH_n , where n is between 2 and 3. It is expressed by the approximate equation:

$$d_{25} = 17 - 2n$$

This equation illustrates the great decrease in density when uranium is converted to the hydride, the density being reduced from approximately 19 to 10.5.

The particle size, porosity, and hardness all militate against successful compaction of uranium hydride by methods used in powder metallurgy. After a large number of trials of various lubricants and additives, it was concluded that the most effective method of forming dense compacts was compression of unlubricated hydride at 100 T.S.I. in a special carbolloy die. Experimental pressures as high as 230 T.S.I. were tried, but the material has almost no tendency to flow or creep, and pressures above 100 T.S.I. have little additional effect. A density of 8.5 g./c.c. and reasonably durable compacts were obtained. It is believed that a slightly bell-tapered, carbolloy die with minimum clearance of the order of 0.0001" would produce satisfactory compacts of $d = 8.5$ with no difficulty. Our studies along this line proceeded only to the point where feasibility was established. Additional details on the effect of lubricants, added ductile metal powders, etc. are given in Topical Report No. 6, Table I. All non-hydrogenous additives, e.g.,

(14) Nottorf, R., MDDB 1585, p 5.

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lead, were found to decrease the N_H from 6.42 to less than 6.0. The N_H was increased by addition of 4% aluminum stearate but not by any other lubricant. It should be pointed out that the theoretical N_H of UH_3 , assuming $d = 10.5$, is 7.93, but that failure to attain maximum density by any feasible means reduces the practical maximum N_H at room temperature to 6.42 for compressed powder. The possibility of using mixtures of powdered uranium metal and pure hydride was considered but not tried in view of poor results with tungsten, etc.

I-2-5 The Pyrophoricity of Uranium Hydride

Uranium, its hydride, and intermediate compositions are extremely pyrophoric, i.e., spontaneously inflammable, when in finely divided form. The pyrophoricity of the powdered metal is to be expected - even finely divided lead powder is pyrophoric; the activity of the hydride is not entirely expected, however, since several other metals lose their pyrophoric properties when hydrided (e.g., Ti, Zr, Ca). A possible reason for the reactivity of UH_3 is evident from the porous, coke-like structure shown by microscopic examination. Moreover when a dozen samples are taken from a batch, some are highly pyrophoric and some are not spontaneously inflammable at all. These pieces of evidence indicate that the inflammability may be due to "hot spots" or discrete particles possessing perhaps pores or areas of high reactivity such that absorption of air raises the temperature locally and results in ignition. This reasoning led to trials of various chemi-sorbable vapors to "poison" or coat such hot spots. A variety of compounds possessing unshared electron pairs were tested and a two and one-half-hour exposure of the hydride to the vapors of diethyl ether, ethylene diamine, isopropylamine, triethylamine, and pyridine completely eliminated pyrophoricity. Hydride so treated could be rubbed on a concrete surface with a steel spatula without ignition. Pellets of treated powder were pyrophoric, however, due presumably to exposure of fresh surfaces. This treatment was very satisfactory, and further studies were not made, although the conclusions reached require confirmation and extension.

I-2-6 Containers for the U-H System

The lower N_H of this system compared to the Ti-H system and the higher dissociation pressure indicates that a more massive container must be employed (see section I-4). Not only must the strength be higher, but also the thickness must be greater to prevent hydrogen loss by diffusion. As in the case cited in I-1-5, a model cylindrical container, whose length is ten times the diameter, was set up and its required wall and end thickness defined by the ASME formula in terms of internal pressure. A tensile strength of 50,000 psi was assumed. The hydride filling was taken to have the theoretical density for any particular composition. The N_H' of the entire unit was then calculated and plotted vs. internal pressure as shown in Fig. (9). The maxima at each temperature thus represent very nearly the best N_H' obtainable for the contained hydride. Actually only 85% of the theoretical density may be easily achieved, hence the N_H' must be corrected to this value. Table VI shows the corrected data.

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Table VI

Maximum N_H ' of Contained U-H System

$T^\circ C$	N_H'
357°	6.80
500°	6.65
575°	6.46
650°	5.95

The fact that a hydrogen concentration gradient will be established along a temperature gradient follows from the data of Figs. (5) and (6). Thus in a container of, say, $UH_{2.9}$, the cold end may reach the composition UH_3 and the hot end will have a composition below $UH_{2.9}$. This gradient will, of course, not be established under the conditions where two solid phases coexist and, therefore, composition is independent of temperature (e.g., at 357° between 20 and 95% theoretical H-content).

I-3 Titanium Borohydride, Thorium Borohydride, and the Attempted Preparation of Tungsten Hydride, Tungsten Alumino and Borohydrides, Iron Hydride, and Nickel Hydride

The advantage of tungsten hydride for NEPA purposes was cited earlier. This compound had never been prepared and recent attempts elsewhere had not been successful(15). Three approaches were attempted in this laboratory: (a) studies of the analogous preparation of iron and nickel hydrides by the Weichselfelder and von Thiede reaction (b) preparation via aluminum hydride and related compounds by metathesis and (c) preparation of tungsten borohydride via sodium and lithium borohydride by metathesis. In the course of these three approaches, it became necessary to study the properties of aluminum hydride and its reactions and also to prepare titanium and thorium borohydrides by the method of Hoekstra and Katz(16). The programs are described in four Topical Reports as follows: No. 3, "Appraisal of the Weichselfelder Method for Preparation of Iron and Nickel Hydrides," July 31, 1950; No. 4, "Aluminum Hydride Etherate," November 20, 1950; No. 7, "The Reactions of Borohydrides and Aluminohydrides with Wolfram (VI) Halides," November 8, 1950; and No. 8, "Preparation and Properties of Thorium Borohydride," November 8, 1950.

I-3-1 The Weichselfelder Preparation of Fe, Ni, W Hydrides

This method(17) involves the reaction of an anhydrous chloride with an ethereal solution of a Grignard reagent in the presence of hydrogen. Presumably the halide is reduced to the colloidal metal which in this active condition combines with hydrogen according to the equation:

(15) NEPA 695-IS-4, July, 1948.

(16) Hoekstra, H. R. and Katz, J. J., J. Am. Chem. Soc. 71, 2488 (1949).

(17) Weichselfelder, T. et al, Ber. 62 B, 769 (1929).

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Although the synthesis has been studied and vindicated by several workers, we have shown that the products are not simple hydrides but unstable, complex compounds containing organic radicals, magnesium, and halogen. No serious study was made of the tungsten compounds, but a considerable effort was made to find conditions which would yield the iron and nickel hydrides as described in the literature. The work was unavailing, and indeed evidence was found that earlier workers may have misinterpreted observations based on hydrogen absorption, etc. A variety of hydrogen-evolving products was obtained in our work, but none gave any indication of the presence of a binary hydride. All were of low N_H , unstable, and pyrophoric.

I-3-2 The Reaction of Tungsten Halides with Aluminum Hydride and Related Compounds

It was hoped that tungsten halides would react with various hydrides according to the equations:

The reaction of WF_6 with AlH_3 under optimum conditions was found to lead to a product having the empirical formula, $\text{WAl}_4\text{H}_{11}\text{F}_{5.5}$. Assuming the fluorine to be present as AlF_3 and the aluminum to be present as AlH_3 polymer, the net formula is $\text{WH}_{2.4}$. Owing to the evident instability of this and the insolubility of AlH_3 and AlF_3 , it was not possible to separate the mixture (or addition compound).

The analogous reaction of WCl_6 with aluminum hydride should yield ether-soluble mixture of AlCl_3 and AlH_3 polymer since AlCl_3 - AlH_3 mixtures are soluble. Unfortunately this did not prove to be the case. After subtracting the calculated amounts of AlH_3 and AlCl_3 from the analysis of the precipitated product, the composition was $\text{WH}_{2.0} - \text{WH}_{3.5}$. This product was also unstable and pyrophoric. In the above two instances, analysis and stoichiometry indicate that one mol of hydrogen is evolved per mol of tungsten present as expected from the equation (2) above. This is evidence supporting the formula, WH_4 . The density of the (unpurified) products was in the vicinity of 1.3 g./c.c., giving an N_H of 5.0. These products were unstable above 60°C in vacuo and were pyrophoric, white powders.

Lithium aluminum hydride proved less satisfactory than aluminum hydride, since lithium halide accompanies the product. Otherwise the reactions followed a similar course yielding slightly less than one mol of hydrogen per mol tungsten halide. It was not possible to ascertain with certainty whether a tungsten hydride or a tungsten aluminohydride was formed. Lithium hydride was found to evolve no hydrogen in contact with ethereal WF_6 , and only what appears to be an etherate of the latter was recovered on filtration and evaporation.

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I-3-3 The Reaction of Tungsten Halides with Lithium, Sodium, and Aluminum Borohydrides

The combination of tungsten, boron, and hydrogen found in $W(BH_4)_4$ would be desirable for NEPA purposes. Accordingly efforts were made to study reactions which might lead to this unknown compound. From the evidence obtained, however, it appears that neither a borohydride nor a tungsten hydride is formed.

The reaction of tungsten halides with sodium and lithium borohydrides was studied in ether, in isopropylamine, and in the absence of a solvent. Preliminary work had shown that diborane and WF_6 did not react at room temperature; thus the dry reaction of WF_6 with $LiBH_4$ could be studied by measuring the amount of the gases hydrogen, B_2H_6 , and WF_6 . Diborane was evolved in an amount only slightly less than equivalent on a molar basis to the tungsten present. Tungsten hexachloride appears to react similarly, and neither yields any identifiable solid product other than a black intractable residue. Sodium borohydride was found not to react with WCl_6 or WF_6 in ether; while in isopropylamine, aminolysis of the halide occurs. Lithium borohydride in ether reacts with WCl_6 smoothly yielding a product from which the lithium chloride could not be separated.

Aluminum borohydride was chosen for the most extensive part of the program because of its volatility. It is a mobile liquid, B.P. 45° , M.P. -65° C. (For preparation see (18)). Details of the reaction with tungsten halides are given in Topical Report No. 7. Aluminum borohydride reacts vigorously with WCl_6 at -65° , presumably according to the reaction:

Simultaneously part of the aluminum borohydride loses hydrogen to form the nonvolatile polymer, AlB_3H_8 . The reduction of the tungsten to the trivalent state is shown by the consistent liberation of $3/2B_2H_6$ per mol W. Sublimation of $AlCl_3$ from the product shows that $1AlCl_3$ is formed per atom W. ($2AlCl_3$ would result if $W(BH_4)_3$ were formed.) Extraction of the solid products was tried. The only known solvent for the AlB_3H_8 polymer is $Al(BH_4)_3$. When the latter was added to the product, however, a further reaction ensued yielding diborane. The solid product had the empirical composition, $WAl_2B_{5.7}Cl_{1.4}H_{13.5}$.

When WF_6 was used in place of WCl_6 , a more vigorous reaction is observed with $Al(BH_4)_3$, probably according to the equation:

The stoichiometry of this equation is confirmed but not distinguished from the less likely equation:

In none of the various combinations tried was any definite evidence obtained for the formation of tungsten hydride or borohydride,

(18) Finholt, A. E., Banus, M. D., Gibb, T. R. P., Jr., Final Report
Contract NOa(s) 9901, December 23, 1949.

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although the latter may be formed as an unstable intermediate and decomposed to form the boride, WB_3 :

I-3-4 Titanium and Thorium Borohydrides

Titanium borohydride was prepared for the sake of experience and nothing significant was added to the work of Hoekstra and Katz (loc. cit.). The program on thorium borohydride was brief but resulted in new data of considerable value. The compound was prepared by reaction of aluminum borohydride with anhydrous thorium tetrafluoride (the latter being excellent material supplied by Dr. F. H. Spedding), according to the idealized equation:

Actually the by-product, instead of AlF_3 , is probably an aluminum fluoroborohydride. Yields of 80% $Th(BH_4)_4$ based on Th were obtained. The product is easily separated from the more volatile $Al(BH_4)_3$ and the non-volatile aluminum fluoroborohydrides by sublimation in vacuo. The purity of products obtained in this way was 98-100%. Resublimation gives large, well-formed crystals approaching 100% purity.

The vapor pressures of $Th(BH_4)_4$ reported by Hoekstra and Katz are 0.05 mm. and 0.20 mm. at 130 and 150° respectively. These authors report the melting point as 203-204° C (with decomposition). Our material did not melt even at 240° C irrespective of the rate of heating. Properties determined are tabulated as follows:

Table VII

Properties of Thorium Borohydride, $Th(BH_4)_4$

Solubility:	Insoluble benzene, tetralin, n-heptane, triethylamine		
	Soluble tetrahydrofuran	23.6 g./100 g.	
	diethyl ether	47.0 g./100 g.	(forms etherate)
Density:	True density 2.59 ± 0.02 g./c.c. at 25° C		
Hydrogen Density:	$N_H = 8.62$		
Thermal Stability:	Stable indefinitely below 150° C in hydrogen. Decomposes irreversibly at 160° C at the rate of 0.01% per hour.		
Stability in Air:	Decomposes slowly (see Fig. (10)). It does not inflame spontaneously below 160° C.		

The rate of decomposition in air of 80% humidity is shown in Fig. (10) with comparison curves from H. I. Schlesinger's laboratory (denoted by asterisks).

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I-4 The Design, Fabrication, Loading, and Testing of Containers

This program includes selection of materials resistant to attack by hydrides at elevated temperatures, impervious to hydrogen, and having a high-tensile strength at 650° C (1200° F); also the design of means for loading containers and sealing hermetically without introduction of air or decomposition of contents. The explosion testing was conducted by Dr. K. Anderson and others at NEPA, but several non-hazardous tests were carried out in this laboratory. The object of the program was to (a) appraise the magnitude of the problem (b) design feasible but not in any sense final types of containers and (c) construct and load several specimen containers.

I-4-1 Selection of Container-Materials - Hydrogen Diffusion Studies

Analysis of published properties of structural materials (apart from flux effects) reveals very few which are resistant to hydrogen embrittlement, hydrogen diffusion, and external oxidation yet which have sufficient mechanical strength at red heat. Of the materials considered, tungsten and molybdenum present fabrication difficulties beyond present facilities. The best compromises were found in the stainless steels, Q-alloy, Monel, and nichrome groups. A tabular summary of the composition and physical properties is given in Tables VIII and IX of Monthly Report No. 6, February 25, 1949. If it is assumed that a tensile strength at 1200° F of about 50,000 psi is required in order that the container not be too bulky, then the only suitable and easily available materials are the stabilized, low-carbon stainless steels and nichrome. Those materials not available in tube form were not considered because of the time and expense required for fabrication. Compound layer tubes, e.g., stainless-molybdenum-stainless, etc. and coated or plated tubes were not considered for the same reason. Materials such as copper, aluminum, etc. alloys are too weak or are attacked by various hydrides (e.g., titanium hydride forms an alloy with copper, etc.).

I-4-2 Measurement of Hydrogen Diffusion at Low Pressure

A number of tubes of alloys selected on the above basis were subject to a rough quantitative study of the hydrogen diffusion rate. It is well known that most metals are permeable to hydrogen at red heat; however, practical data are not available. One method employed in this laboratory consisted of measuring with a mercury slug flowmeter the flow of hydrogen into a heated tube of the metal being tested. The equipment is shown in a figure on p 5 of Monthly Report No. 3, November 25, 1948. The heated area was sharply defined by water jackets soldered to the tube at the edge of the furnace zone.

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The results of this study are shown in Table VIII. It was found that the rate of diffusion is substantially independent of pressure over the range 76-117 cm. within experimental accuracy. The principal factor affecting diffusion rate is the length of time the metal is heated in contact with hydrogen. All diffusion rates declined from original high values to very low values over a period of days. The magnitude of this effect is quite remarkable and in one instance (Progress Report No. 4, Table II), a decline of nearly one hundredfold was observed. The values cited in Table VIII are very encouraging. While the diffusion rates are far lower than predicted from analogous data⁽³⁾, the very fact that they are low supports their accuracy, since losses other than by diffusion would give high results.

I-4-3 Measurement of Hydrogen Diffusion at Higher Pressures

In addition to the low-pressure studies on seamless tubing, investigations were made of diffusion losses from welded cylinders at 100-1000 cm., 650-800° C. These cylinders were constructed from "seamless" (actually factory welded and re-extruded) tubing by welding press-fit ends by atomic hydrogen. A medium-wall capillary tube was welded to one end and diffusion losses through it were ignored, although they undoubtedly added to the total loss. The latter was calculated from the pressure drop observed and the known volume of the system. That the method employed actually measures hydrogen loss was confirmed by a single experiment in which the hydrogen which had diffused through the shell was measured by a pressure increase method. Good agreement was obtained (Progress Report No. 7, p 15). The cylinders are described in Progress Reports No. 8 (Fig. 1) and No. 6 (Fig. 2). It was observed that end plates cut from bar stock were very permeable, due to axial flaws and all studies of cylinders having such ends were discarded. Ends were cut from flat stock for all other cylinders. Table IX shows that the rates of diffusion at moderate pressure are relatively low and indeed comparable to those reported in the preceding table despite the difference in pressure. This does not indicate that diffusion rate is substantially independent of pressure, however, for the discrepancy may be attributed largely to a thickness and fabrication factor. The low-pressure tests were made with thin-wall seamless tubing and the high-pressure tests with larger diameter, thicker tubing. Variations in metal quality must also be taken into account. As noted in the tables, the data shown have been corrected to a thickness of 1 mm. by multiplying the observed diffusion by the average wall thickness in millimeters. This assumes that diffusion rate is inversely proportional to thickness. The variable relation of diffusion rate and pressure is shown in Figs. (11) and (12). The reason why alloy 316 shows a linear relation is not clear. Theoretically the square root relation should be followed as in Fig. (12).

I-4-4 Results of Diffusion Studies

Derivation of an overall diffusion equation relating rate to temperature, pressure, and wall thickness requires additional data in view of the above considerations. Such an equation has been worked out for molybdenum, using the data of Smithells⁽¹⁹⁾. The equation is plotted

(19) Smithells, C. J., "Gases and Metals," John Wiley & Sons, Inc., New York, 1937.

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Table VIII

Hydrogen Diffusion Constants for Seamless Tubes
at 76-117 cm. Pressure (corrected to STP)

Material	Hours Heated	T°C	cc/cm ² /mm/hr	Remarks
316	24	650	.15	
	168	650	.07	
	240	650	.03, .05	
	264	650	.03, .04	
	504	650	.02, .009, .03	
347	96	650	.1	
	192	650	.35*	*8 days at 800° C in- cluded in no. of hours.
	120		.04	
	288	650	.06, .02	
	384	650	.01(6)	
304	5	800	.17	
	28	650	.02, .13	
	73	650	.003, .04	
	76	800	.03	
	94	800	.04	
	97	650	.009	Cooled, ex- posed to air, then reheated 3 hrs.
	240		.003	
Nichrome	24	650	.12	
	72	650	.07	
	120	650	.06	
	240	650	.002	Part of time at 800° C.
Nichrome V	3	650	.12	
	24	650	.13	
	120	650	.05	
	180	650	.03	
	300	650	.003	
Aluminum 2S	48	550	nil	

Table IX

Hydrogen Diffusion Constants for Stainless Steel
Welded Cylinders at Various Pressures and Temperatures

Material	Hours Heated	T°C P _{cm}	cc/cm ² /mm/hr
316	24	800 840	.005, 0.14
	24	800 368	.003
	2	800 400	.01, .01, .04
347	194	650 1000	.04, .02

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in Fig. (13). The vertical scale represents diffusion rate in cc/sec/cm²/mm corrected to STP. Stainless steel should yield a similar relation, but it is not possible to evaluate the constants accurately because of the above-mentioned time factor.

The information contained in Tables VIII and IX and Fig. (13) indicates that the diffusion problem is not as serious as was once believed. The per cent loss of hydrogen from a contained hydride in a vessel meeting ASME specifications will be an extremely small fraction of a per cent from a molybdenum container as shown in Table X. The loss from a similar 347 or 316 stainless steel container will be larger. Thus for a 347-alloy cylinder of 120 cc internal volume, 141 cm² area, with an average wall thickness of 2 mm., the hydrogen loss from Table IX at 650° C 1000 cm. pressure will be about 3 c.c. per hour, or 3000 c.c. in 1000 hrs. If this cylinder contained 375 g. of TiH₂, say, whose hydrogen content is 168,000 c.c., the per cent loss of hydrogen is only 1.7% in 1000 hrs.

The effect of annealing, quenching, and cold-working metals on their permeability is discussed in a recent article by Smith⁽²⁰⁾. The large effect of ionization of the hydrogen (by a glow discharge) has been observed by Russel⁽²¹⁾. Ionization evidently increases permeability of aluminum very greatly and this phenomenon requires further study.

Table X
Diffusion Losses from Cylindrical Molybdenum Containers
of Various Dimensions

(Length = 10 D) at Various Temperatures and Pressures

Diam. D	Area Inside 10.5 D ²	Volume Inside 2.5 D ³	Press. cm.	Wall Thickness required by ASME formula mm.	Temp. °C	H-loss g/100 hrs.	H-loss in grams per unit volume per 100 hrs.
10	3,300	7,860	10 ³	.214	600	2.2-8	2.83-12
10	3,300	7,860	10 ⁴	2.19	600	6.75-9	8.58-13
10	3,300	7,860	10 ⁴	2.19	800	3.94-5	5.0-9
10	3,300	7,860	10 ⁵	28.70	600	1.63-13	2.07-17
20	13,200	62,850	10 ³	.428	600	4.39-8	7.0-17
20	13,200	62,850	10 ⁴	4.38	600	1.35-8	2.14-13
20	13,200	62,850	10 ⁴	4.38	800	7.4-5	1.18-9
20	13,200	62,850	10 ⁵	57.4	600	3.27-9	5.2-14
40	52,770	503,000	10 ³	.856	600	8.77-8	1.74-13
40	52,770	503,000	10 ⁴	8.76	600	2.81-8	5.6-14
40	52,770	503,000	10 ⁴	8.76	800	1.48-4	2.84-10
40	52,770	503,000	10 ⁵	115.0	600	6.52-9	1.3-14

(20) Smith, D. P., Science 113, 348 (1951).

(21) Russel, A. S., Metal Progress 55, 827 (1949).

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I-5 Recommendations for Further Work

A number of significant problems have been raised by the work on metallic hydrides. Of particular interest is the problem of radiation stability. Since extremely pure hydrogen and pure titanium combine rapidly, it is probable that radiation will not have a cumulative effect beyond that expected (by analogy with water). Minute amounts of impurity were found to have a profound effect on equilibrium pressures and on recombination. This undesirable effect requires far more study. In two instances, however, an impurity was found to have a beneficial effect, viz., traces of nitrogen increased the hydrogen content of the Ti-H system over a low range of compositions, and nickel was found to increase the ability of zirconium to retain hydrogen. These observations necessitate an examination of such ternary systems to see if a third constituent may prove desirable. A theoretical approach via Pauling's method is recommended. This program would include mixtures of hydrides, e.g., $\text{CaH}_2\text{-UH}_3$, as well.

The problem of tungsten hydride is not yet resolved and requires additional study as does the matter of complex nickel and iron hydrides.

While this laboratory has no especial desire to study hydrogen permeability, a great deal of further work on this problem is required. Such matters as fabrication of molybdenum, etc. in a massive form impervious to hydrogen would come under this heading, as well as the development of additional impervious metals and alloys. The plating of containers by molybdenum or tungsten alloys is possible by known means and should be explored.

The properties of metal-hydrogen solid systems containing relatively small amounts of hydrogen are almost entirely unexplored and call for further study in view of the fact that a matched shield may not require a stoichiometric or high-composition hydride.

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Part II

Light Hydrides for Cool External Shielding

The need for an external neutron shield of minimum weight and bulk was cited in the introduction. A purely geometrical method of calculating the weight efficiency of various hydrogenous materials relative to water was devised by Dr. V. P. Calkins and modified by this laboratory. Such an external shield need not be exposed to temperatures above 200-300° C and must have a maximum hydrogen content on a weight basis. Therefore, the criterion is not N_H but a factor involving a maximum hydrogen percentage and a minimum density.

II-1 The Geometrical Calculation of External Shield Weights Relative to Water

It may be shown⁽⁸⁾ that the weight of an annular external shield containing MH_n relative to a water shield containing the same number of hydrogen atoms is given by the equation:

$$W_{MH}/W_{H_2O} = kE^2/d$$

where W_{MH} = weight of shield

W_{H_2O} = weight of water shield

E = molecular weight of MH_n divided by n . (This is referred to as the "Hydrogen Equivalent Weight" or "H.E.W.")

d = density (g./c.c.)

k = constant equal to .0123 for an annular cylindrical shield.

The order of merit of various hydrogenous materials is, therefore, equal to E^2/d which is related to N_H (no. H atoms per c.c. times 10^{-22}) by the equation:

$$E^2/d = 60.6E/N_H$$

Thus to find the shield weight relative to water, it is necessary to determine only the per cent by weight of hydrogen ($E = 100\%$) and the density and employ the above equation. Table XI lists this shield weight ratio for a number of common and uncommon materials.

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Table XI

Compound	E ² /d	$\frac{V_{MH}}{V_{H_2O}}$
CH ₄ at B.P.	38.74	.485
NH ₃ at B.P.	39.50	.487
LiBH ₄	43.60	.571
B ₄ H ₁₀	50.90	.628
B ₂ H ₆	44.50	.649
N-n,dimethyl valeramide	51.45	.671
n-pentane	57.50	.714
n-amyl amine	58.00	.719
N ₂ H ₄	63.40	.763
dimethyl n-amyl amine	61.90	.781
B(CH ₃) ₃	61.70	.787
NH ₄ F	65.40	.786
Al(BH ₄) ₃	65.30	.833
N ₂ H ₄ ·H ₂ O	67.50	.826
n-amyl alcohol	66.20	.840
Si(C ₂ H ₅) ₄	68.40	.847
Ge(C ₅ H ₁₁) ₄	72.10	.893
Ge(C ₂ H ₅) ₄	74.50	.917
LiH	77.10	.940
B(OC ₅ H ₁₁) ₃	77.50	.970
B ₅ H ₉	80.80	1.000
Ge(C ₃ H ₇) ₄	80.01	1.000
H ₂ O	81.2	1.000
NH ₄ H ₂ PO ₂	76.25	1.005
n-valeramide	82.70	1.020
Sn(C ₅ H ₁₁) ₄	82.30	1.026
B(OC ₄ H ₉) ₃	84.20	1.046
Si(CH ₃) ₄	83.00	1.046
(C ₆ H ₁₃) ₃ B ₃ O ₃	83.60	1.061
LiAlH ₄	95.3	1.176
SiH ₄	94.6	1.190
C ₆ H ₅ (CH ₂) ₃ CH(CH ₃) ₃	98.30	1.204
methyl valerate	103.00	1.282
Ga(C ₂ H ₅) ₃	103.50	1.287
B(OC ₂ H ₅) ₃	108.25	1.381
Ge(CH ₃) ₄	121.60	1.552
Zn(C ₂ H ₅) ₂	129.00	1.666
(NH ₄) ₂ SO ₄	154.30	1.923
Pb(C ₂ H ₅) ₄	157.70	2.000
TiH ₂	155.00	2.000

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II-2 Lithium Borohydride

The high order of merit for this compound suggested that its properties be ascertained. Lithium borohydride was first prepared by Schlesinger and Brown(22). This laboratory has studied the preparation of the compound independently of SC-2026 and employed its method for the preparation of high-purity material. When pure the compound is not spontaneously inflammable, although in loose powder form, it deteriorates very rapidly in moist air. We have found the melting point to be 286°C with slow decomposition and have found the density to be 0.686 g./c.c. at 25°C (compared with 280° and 0.680 reported by Schlesinger and others). Pellets were prepared by compression at low pressures in a carbolloy die and found to have theoretical density. Several small castings were made in pyrex. It was found possible to cast the material in hydrogen by dropping the powder through a glass tube, the lower end of which was heated by a narrow annular coil. The coil was raised slowly as the material deposited. This technique gave durable translucent pellets of theoretical density. The pure substance is thermally stable over short periods of time at 250°C . A planned program on thermal stability was put aside for more pressing matters and never resumed. A number of mixtures with low-melting organic solids was made in the hope of lowering the casting temperature, and the possibility that solutions of LiBH_4 in liquid ammonia would have a high order of merit was considered. Both projects were commenced but were terminated immediately in favor of a program on quaternary borohydrides.

II-3 Tetraalkylammonium Borohydrides

The possibility of forming ammonium borohydrides was discussed with NEPA in 1949, but not pursued because of the predicted instability at 650°C . Thus Schaeffer and Anderson(23) present evidence that mono-, di-, and trimethyl ammonium borohydrides must be unstable even at low temperatures. Cursory work by Winternitz(24) indicated that an aqueous solution, presumably containing a quaternary or tetramethyl ammonium borohydride, was stable. Since none of this series of compounds had been prepared in a pure state to our knowledge, this laboratory commenced a synthetic program which proved highly successful. Three quaternary borohydrides were prepared by several different and practical syntheses, and the properties determined. Two of these compounds are described in Table XII with LiBH_4 as a reference. The third ammonium borohydride (benzyltrimethyl) contained a bulky hydrocarbon group and had an inferior order of merit. The weight ratio shown in the last column illustrates that external shields of either of the ammonium borohydrides weighs less than half as much as a water shield. From Table XI it may be calculated that the $(\text{CH}_3)_4\text{NBH}_4$ shield has only 66% the weight of a pentane shield. Moreover it is a stable solid at temperatures where pentane exerts a large vapor pressure. Tetramethylammonium borohydride has the highest order of merit of any reported substance. Work on related substances such as hexamethylethylenediammonium diborohydride, $\text{H}_4\text{B}(\text{CH}_3)_3\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_3\text{BH}_4$, hydrazonium borohydride, $\text{NH}_2\text{NH}_3\text{BH}_4$, s-dimethylhydrazonium diborohydride, $\text{H}_4\text{BCH}_3\text{NH}_2\text{NH}_2\text{CH}_3\text{BH}_4$, guanidonium borohydride, $\text{NH}_2\text{C}(\text{NH})\text{NH}_2\text{BH}_4$, etc.

(22) Schlesinger, H. I. and Brown, H. C., J. Am. Chem. Soc. 62, 3429 (1940); also U.S. 2,461,661.

(23) Schaeffer, G. W. and Anderson, E. R., J. Am. Chem. Soc. 71, 2143 (1949).

(24) Winternitz, P., "A Brief Report on Present Activities of Reaction Motors, Inc.," September 3, 1950.

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was not commenced in view of the assignment of priority to the program reported in Part III.

Table XII

Compound	Density	wt. % H	N _H	E ² /d	W _{MH} /W _{H₂O}
(CH ₃) ₄ NBH ₄	0.813	18.0	8.86	38.0	.471
(C ₂ H ₅) ₄ NBH ₄	0.927	16.6	9.29	39.3	.484
LiBH ₄	0.686	18.3	7.34	43.7	.571

II-3-2 Thermal Stability of Tetramethylammonium Borohydride (TMAB)

The rate of decomposition of TMAB on heating at various temperatures in evacuated pyrex tubes was ascertained by measuring the pressure developed (Topical Report No. 9). The per cent decomposition per hour is shown in Table XIII.

Table XIII

Thermal Decomposition of TMAB

Temp. °C	% Dec. per hr.
150	0.095
175	4.1
195	33.3
225	250

This indicates that the pure material may not be used over 150° C in contrast with LiBH₄ which is stable (at least qualitatively) at 250° C.

On heating in vacuum over several hours at 220-225° C, the compound decomposes almost completely according to the equation:

The resulting trimethylamine borine has been obtained in 96% yield and identified by its M.P., 93-4° C, and analysis. Small amounts (4%) of trimethylamine and a 2% non-volatile residue were found.

II-3-3 General Properties of TMAB and Solutions

Tetramethylammonium borohydride is a white, microcrystalline material easily handled in air but deteriorating on contact with humid air. It burns quietly with a green flame when ignited but cannot be ignited by friction. When heated to 150-250° C on a metal block, it decomposes to volatile materials without ignition. The following

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solubilities are reported in g./100 g. solvent at the temperature indicated: water 20°, 48; water 40°, 61; ethanol 25°, 0.5; 95% ethanol 25°, 1.42; acetonitrile 25°, 0.4. It is insoluble in diethyl ether, isopropylamine, pyridine, chloroform, dioxane, tetrahydrofuran, ethyl cellosolve, and N-methyl morpholine. It reacts with lower alcohols.

The material is easily compacted at or below 255 TSI to give hard, durable, and translucent pellets having a density of 0.766 g./c.c. (94% of theoretical). A pellet containing 10% powdered tungsten had a density of 0.842 g./c.c., showing that the tungsten had no voids not filled.

Water solutions of TMAB were studied. At 25° C the saturated solution contains 48 g./100 g. water and has a density of 0.906 g./c.c. The solution appears stable. The greater solubility at 40° C is accompanied by a slow evolution of hydrogen. The rate of decomposition is 0.04% per hour which, however, could be reduced to 0.02% or less by addition of $(\text{CH}_3)_4\text{NOH}$. The solution contains 61 g. per 100 g. water, has an N_H of 7.33, and the shield weight is 75% that of a water shield.

II-3-4 Preparation of Tetramethyl, Tetraethyl, and Trimethylbenzylammonium Borohydrides

The general method is metathetical based on the reaction:

Solvents are water, aqueous alcohol, absolute alcohol, and isopropylamine. The designation M refers to Na or Li and X may be a halide, hydroxide, phosphate, carbonate, acetate, or oxalate ion. The choice of solvent depends on the reactivity of MBH_4 and on the solubility. It is essential that one of the products be less soluble than either reactant.

Of the many preparations carried out (see Topical Report No. 9 and Progress Report No. 29, p 2), the two best for TMAB are (a) the reaction of the quaternary hydroxide with sodium borohydride in aqueous solution followed by evaporation and extraction of the NaOH by 95% alcohol and (b) the reaction of the quaternary fluoride with lithium borohydride in ice water.

The latter reaction is also preferred for the tetraethyl and trimethylbenzyl compounds. The quaternary fluorides are easily prepared from the available hydroxides by titration with hydrofluoric acid. Alternatively the quaternary iodide is easily converted to the fluoride by use of (soluble) silver fluoride. Details of a few selected methods are as follows:

This compound has been prepared in a high degree of purity from a 10% solution of the quaternary hydroxide and NaBH_4 by the reaction:

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(1)	$(\text{CH}_3)_4\text{NOH (sln.)} + \text{NaBH}_4 \longrightarrow (\text{CH}_3)_4\text{NBH}_4 + \text{NaOH}$			
Sol. in H_2O	extremely	55 g./100 g.	48 g./100 g.	109 g./100 g.
Sol. in 95% alcohol	extremely	4 g./100 g.	1.4 g./100 g.	15 g./100 g.

In the first method 4.2 g. (.11 mol) of NaBH_4 were added to 100 g. of a 10% solution of $(\text{CH}_3)_4\text{NOH}$ to give a nearly clear solution. After centrifuging the solution was evaporated at room temperature with stirring on the vacuum line until a large crop of crystals had formed and there was only a small amount of syrup. These crystals were filtered at about 10°C and washed with a few c.c. of ice water. On drying in a good vacuum at $70-80^\circ\text{C}$ for an hour, there were 4 g. of product which analyzed 94% $(\text{CH}_3)_4\text{NBH}_4$. Further evaporation of the mother liquor and wash gave another crop of crystals which on drying analyzed 94% also. There was .55% Na in this material, showing that the metathesis was substantially complete. The B:H ratio was only 1:3.6. Complete analysis showed that this was due to borate which was the main impurity. The yield was only 61%.

When the solubility of the quaternary borohydride in 95% alcohol had been determined, a new method of purification was developed whereby the solution was evaporated dry and the NaOH was leached out along with most of the NaBO_2 by 95% alcohol. In a larger-scale run, 8.5 g. (.22 mol) of NaBH_4 were added to 200 g. of 10% $(\text{CH}_3)_4\text{NOH}$ solution which had been evaporated to 100 c.c. Air and CO_2 were excluded from this run. The solution was evaporated dry on the vacuum line. The solid was extracted with 90 c.c. of 95% alcohol and suction filtered. The crystals were washed twice with 50 c.c. portions of cold alcohol, then vacuum dried at $70-80^\circ\text{C}$ for 18 hrs. The result was 18.5 g. of 99+% pure $(\text{CH}_3)_4\text{NBH}_4$ (93% yield). Analysis:

	Found	Theory
B	12.13%	12.17%
H(ev.)	4.49%	4.50%
C	52.4 %	53.9 %
H(total)	17.9%	18.1%
N	16.4 %	15.8 %
Na	.6 %	0.00%

B:H* = 1:3.98 C:H** = 1:3.04 B:C = 1:3.9

* Hydride ** Organic

This material was kept in a screw-capped bottle for several months with no detectable decrease in purity. Most of the physical measurements and thermal decomposition data were obtained using this material. It is interesting to note that the quaternary borohydride is less soluble in alcohol than is saturated in NaOH. The theoretical amount of quaternary borohydride dissolved by the 190 c.c. of alcohol

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was 2.2 g. but only 1.5 g. went into solution. In another case where there was only a single wash, this lowering of the solubility of the borohydride was even more marked.

At present this method appears the most practical for the preparation of $(\text{CH}_3)_4\text{NBH}_4$, since the quaternary hydroxide is commercially available, and there is no difficulty in preparing aqueous solutions of NaBH_4 even on a large scale. The chief difficulty lies in the length of time necessary for evaporating the water from the reaction mixture.

$(\text{CH}_3)_4\text{NBH}_4$ Preparation from $(\text{CH}_3)_4\text{NF}$ and LiBH_4

Aqueous solutions of tetramethylammonium fluoride were prepared by two methods. The first involved the neutralization (to a pH of 9-10) of 48% hydrofluoric acid with tetramethylammonium hydroxide; the second involved the metathetical reaction of soluble silver fluoride with aqueous tetramethylammonium chloride, bromide, or iodide with the precipitated silver chloride, bromide, or iodide removed by filtration. The latter novel method is preferred by us because it avoids the hydroxide and the consequent dangers of contamination with carbon dioxide, silicates, and borates. A measured portion of the tetramethylammonium fluoride solution was then mixed with an aqueous solution of a stoichiometric amount of lithium borohydride, prepared by adding ice water to chilled lithium borohydride powder in a nitrogen atmosphere. The precipitated lithium fluoride was removed by filtration through a medium porosity sintered glass funnel and the water was removed from the clear filtrate by vacuum at room temperature. The resulting solid cake was then taken up in a minimum amount of water, filtered again, and the filtrate dried as before but with a final heating at 100°C for three hours. Material prepared in this manner analyzed 95.0% by hydrogen liberated on acid hydrolysis. The chief impurity was borate which could be removed by an alcohol leach as above.

$(\text{CH}_3)_4\text{NBH}_4$ Preparation from $/(\text{CH}_3)_4\text{N}/_3\text{PO}_4$ and LiBH_4

Tetramethylammonium phosphate was prepared in the following manner: Approximately 10 N phosphoric acid was standardized by titration to the methyl red and phenolphthalein end points. Equimolar amounts of the phosphoric acid and tetramethylammonium hydroxide were then measured from burettes and mixed to give (presumably) the triphosphate with a pH in the range of 13. The tetramethylammonium phosphate solution was then mixed with a stoichiometric amount of aqueous lithium borohydride. The precipitate was removed by filtration and the clear filtrate evaporated in vacuum and heated at 100°C for three hours. The product analyzed 78.7% by hydrogen liberated with acid hydrolysis. The hydrogen to boron ratio of 3.37 indicated that the chief impurity was borate which could be removed by an alcohol leach.

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$(CH_3)_4NBH_4$ Preparation from $[(CH_3)_4N]_2CO_3$ and $LiBH_4$

Carbon dioxide was bubbled into tetramethyl ammonium hydroxide to the discharge of the phenolphthalein color. An equal amount of the quaternary base was then added to convert the bicarbonate to carbonate. The resulting solution was then mixed with a stoichiometric amount of aqueous lithium borohydride, and the mixture was evaporated to dryness in vacuum. The resulting white cake was taken up in a minimum amount of water and the precipitated lithium carbonate removed by filtration. The clear filtrate was evaporated to dryness in vacuum and heated at 100° C for three hours. The product analyzed 88.7% by hydrogen liberated on acid hydrolysis. There was 1.1% lithium but the chief impurity was borate.

$(CH_3)_4NBH_4$ Preparation from $[(CH_3)_4N]_2C_2O_4$ and $LiBH_4$

Tetramethylammonium oxalate was prepared by the neutralization of a weighed amount of oxalic acid crystals with standard tetramethylammonium hydroxide. A slight excess of the base was added to obtain a pH of 10. This solution was mixed with a stoichiometric amount of lithium borohydride solution and the mixture evaporated to dryness in vacuum. The resulting cake was taken up in a minimum amount of water and the lithium oxalate removed by filtration. The clear filtrate was evaporated to dryness in vacuum and heated at 100° C for three hours. The product analyzed 72.3% by hydrogen liberated on acid hydrolysis. It contained 10.0% lithium oxalate in good agreement with the 10.9% to be expected on the basis of the relative solubilities of lithium oxalate and tetramethylammonium borohydride. There was considerable borate present as evidenced by the low-active hydrogen to boron ratio of 3.50.

$(CH_3)_4NBH_4$ Preparation from $[(CH_3)_4N]_3PO_4$ and $NaBH_4$

Tetramethylammonium phosphate was prepared as above and evaporated to a thick syrup in vacuum. A stoichiometric amount of 95% sodium borohydride was dissolved in a minimum amount of water and the solutions mixed and chilled in an ice bath. The mixture was filtered at 0-2° C and the clear filtrate evaporated in vacuum and heated at 100° C for three hours. The product analyzed 90.0% by hydrogen liberated on acid hydrolysis. The phosphate content was 10%, the low purity being due to borates.

$(CH_3)_4NBH_4$ Preparation from $[(CH_3)_4N]_2C_2O_4$ and $NaBH_4$

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Tetramethylammonium oxalate was prepared as above and mixed with an aqueous solution of a stoichiometric amount of 95% sodium borohydride. The mixture was evaporated in vacuum to a cake, taken up in a minimum amount of water, and filtered to remove the sodium oxalate. The clear filtrate was evaporated in vacuum and heated to 100° C for three hours. The product analyzed 78.9% by hydrogen liberated on acid hydrolysis. It contained 6.83% sodium oxalate which agrees well with the expected 6.4% based on relative solubilities. The hydrogen to boron ratio was 3.52, indicating the remaining impurity was largely borate.

The large-scale preparation of quaternary ammonium borohydrides appears to present no major difficulties and the raw materials, NaBH_4 or LiBH_4 and quaternary hydroxides, are available commercially. Work by this laboratory on the solubility of the quaternary halides, and lithium and sodium salts in various liquids paves the way for further studies and development of large-scale synthesis (see monthly Report No. 29, p 2).

II-3-5 Trimethylamine Borine

As noted above TMAB decomposes on heating to yield trimethylamine borine, $(\text{CH}_3)_3\text{NBH}_3$. This compound is volatile, melts at 93° C, and is evidently much more stable thermally than TMAB. Its density was found to be 0.84 at 25° C. It does not react with air or moisture during handling and is sufficiently waxy to permit compression to theoretical density or casting. The N_H is 7.75 and the order of merit 51.2 which gives a shield weight 63% that of an equivalent water shield.

II-4 Recommendations for Further Work

The whole group of quaternary ammonium borohydrides awaits development. It is recommended that this work be intensively pursued not only for NEPA purposes, but for other potential applications as well. Certain cyclic or bridge compounds of this type may have a better order of merit than TMAB and a higher thermal stability. The derivatives of borine are equally worthy of additional study as evidenced by the desirable properties of trimethylamine borine.

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Part III

Hydrides as Moderators

The potentialities of thermally stable light-metal hydrides for use as fluid moderators was suggested to this laboratory by Dr. Calkins several months prior to termination. The presence of hydrogen in a fluid homogenous fuel system would, of course, be very advantageous. Since no data whatsoever existed on the properties of light-metal (alkali and alkaline earth metal) hydrides up to 1000°C , it became necessary first to acquire this basic data as quickly as possible. The next step required a study of binary mixtures of hydrides with fluorides, nitrides, carbides, and hydroxides. This latter phase was only partially completed and the third phase dealing with ternary systems was not commenced. In appraising the very interesting results obtained, it should be borne in mind that the field is broad and that each phase was barely touched upon in this program.

III-1-1 General Considerations

Hydrides for use in moderators must not contain elements undesirable by reason of nuclear properties (e.g., Li, Cl, Br, I, etc.), nor must they develop unduly high thermal dissociation pressures. The dissociation must be readily and rapidly reversible and radiation must not have an irreversible effect, i.e., rapid recombination is essential. For some purposes a homogeneous molten system is desirable, whereas a solid system is required for other designs. In a solid system the distribution of solid phase hydrogen along a thermal gradient must be taken into account if a less-than-stoichiometric hydride is present. The hydride system must be non-corrosive toward permissible materials of construction.

The saline hydrides of the first two periodic groups appear most suitable from the point of view of stability. Lithium hydride is the only member of the series which melts without substantial dissociation below 1000°C . No other hydride is reported to melt. Hydrides of the saline type are similar in many respects to chlorides and it follows that mixtures of hydrides with each other or with halides might show eutectics in the same way as mixtures of halides. This would lead to molten systems containing a high proportion of hydrogen. However, fluorides, the only permissible halides, have much higher melting points than chlorides; hence hydride-fluoride mixtures may not be suitable. Moreover in mixed systems of the type NaF-CaH_2 , a metathesis may be expected to take place with formation of some NaF which is far less stable thermally than CaH_2 .

The program whose results are reported below was terminated when about half complete. However, the information is new and covers a considerable number of systems. Equilibrium pressures of hydrogen over Li, Na, Ca, Sr, Ba and Li-LiF, Na-NaH, Na-NaOH, Na-NaF, Ca-CaC₂, Ca-Ca₃N₂, and Ca-NaH systems have been measured for one or more metal-hydrogen ratios. The equipment used is the same as employed for the Ti-H studies reported in Part I. The technique, however, is different. The observed pressure of hydrogen over the system at any temperature is taken to be the equilibrium pressure and no correction is made for the small free

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volume of the container, tubing, and gauge. Thus 100% CaH_2 on heating in an evacuated system eventually dissociates to give a pressure of, say, 500 psi. By this dissociation the composition of the solid phase is reduced to perhaps 99%, since 1% of the original hydrogen is now in the gas phase. This small error in the composition may be allowed for, but the calculations are very time consuming. We have chosen to neglect this factor in order to permit submission of this report. The data are available and the small corrections may be computed at some future time. However, the excellent agreement between our data and extrapolated data of earlier workers in the Na-H and Ca-H systems indicate that this error is negligible.

III-1-2 The Lithium-Hydrogen System

Selected lots of Lithalloys' regular grade lithium were cut under argon and hydrided at 720°C to give a nearly white crystalline material analyzing 98.5-99.0% LiH (by evolution analysis). The original content of carbon (0.35%) was reduced to nil during the dissociation studies reported below, and the original nitrogen content of 0.6% was reduced to 0.2%. The material contained spectrographic traces of sodium, potassium, and calcium, the latter disappearing during runs. Traces of Ni but no Cr or Fe were picked up during the runs from the 347-alloy stainless steel containers which showed a slight attack by the molten hydride. Metallurgical examination reveals formation of a roughened layer on the 347-alloy interior surface after 150 hrs. at temperatures ranging up to 1050°C . This layer is approximately 0.01 mm. thick.

The dissociation runs were carried out using the equipment and technique described above. Temperatures were measured with a chromel-alumel thermocouple in a stainless steel well protruding through the cover of the cylindrical bomb down into the contents. Results are presented in Figs. (14) and (15). The logarithmic method of plotting is a better test of the data and indicates a family of straight lines whose slope varies with composition. The latter is shown as per cent of stoichiometric hydrogen content (LiH = 100%) in Fig. (15). (These percentages are based on analysis and if the impurity is completely inert, the 98.5% curve would be equivalent to a 100% curve.) The free volume of the measuring system was 83 c.c., of which 9 c.c. were in the gauge line and 19 c.c. for the bomb and its stem.

These results are considerably higher than those recalculated from W. C. Johnson's data⁽²⁵⁾ and shown in Fig. (16). The reason for the discrepancy is not fully understood, but the data of Fig. (15) represent measurements made on commercially pure material, whereas Johnson's work was carried out with exceptionally pure material.

Melting was observed at 680°C in agreement with published data. No melting of a separate Li phase was observed at 186° (M.P. of Li metal).

(25) Johnson, W. C., Chem. Thesis of M. R. J. Perlow, University of Chicago, December, 1941.

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III-1-3 Lithium Hydride-Lithium Fluoride

An intimate mixture of 18.7 g. 99% LiH and 12.08 g. Harshaw "Optical Quality" LiF was studied. The molar ratio is 5.85 LiH to 1 LiF. On heating a slight pressure developed at 375° C and then dropped to an unreadable value. On increasing the temperature dissociation occurred giving the data shown in Fig. (17) (see Progress Report No. 30, p 3). A poorly defined plateau was observed in the thermocouple record on heating and on cooling close to 680° C. On opening the shell it was found that melting had occurred, since the contents consisted of large, opaque, cream-colored crystals. A superficial deposit of golden metallic material was observed.

Evidently LiF forms a solid solution with LiH having a lower dissociation pressure than LiH alone. This system is fusible, but there is no evidence that it gives a homogeneous melt.

III-2-1 Sodium Hydride

Sodium hydride was prepared from 99.9% metal and hydrogen by agitating the molten metal at 300-400° C, 200 psi of hydrogen. The product was a white powder analyzing 99+% NaH (by evolution). Owing to the tedious necessity of handling this material entirely in argon, an attempt was made to prepare it in the stainless steel bomb used for dissociation runs. It was found that molten sodium did not combine with hydrogen up to 625° C and up to 400 psi pressure of hydrogen. This is a most significant observation, since it leads inescapably to the conclusion that the dissociation is not reversible. This conclusion is supported by the dissociation studies.

The latter were conducted as usual. It was found that the technique gave results for 100% hydride in complete agreement with the data of Keyes(26) and Herold(27), as shown in Fig. (18). For lower compositions, however, anomalies were observed as shown in Fig. (19). Not only was the dissociation irreversible, but over certain ranges was nearly independent of temperature as evidenced by the reproducible plateaus. After a run traversing a plateau, a residual pressure was always noted on cooling. If the bomb was reheated, the plateau could be retraced. However, if the small pressure was bled off after cooling, a lower plateau was found. The contract was terminated before this anomaly could be studied. The possibility that the plateaus continue up to temperatures of 1000° C is most interesting. The bomb contained 52 g. of NaH and had a free volume (including gauge and tubing) of 100 c.c.

No evidence of melting was found even at compositions below Na₂H. An inflection occurred at 95° C, presumably due to sodium but no fusion was noted below 840° C.

(26) Keyes, F. G., J. Am. Chem. Soc. 34, 779 (1912).

(27) Herold A., Compt. rend. 228, 686 (1949).

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III-2-2 Mixtures of NaH with CaH₂, NaOH, NaF

The following mixtures were prepared by mixing the scrupulously dried compounds with 1 mol NaH in dry argon and loaded into cylindrical bombs:

Compound	Source	Analysis	Mols per mol NaH	Tot. wt. Mixt.
CaH ₂	M.H.I.	99+%	1.0	62 g.
NaOH	Baker's C.P.	—	0.98	57 g.
NaF	Gen. Chem. Co. C.P.	—	0.50	44 g.

These mixtures were degassed in the bombs for 16 hrs, the NaH-NaF and NaH-CaH₂ at 210° C, 3 mm., and the NaH-NaOH at 230°, 0.5 mm. Dissociation runs were then carried out with the results shown in Fig. (20). Except for the NaH-NaOH mixture, there was no substantial departure from the pure NaH curve. The NaOH-NaH mixture shows a lower dissociation pressure and flattens out at 640° C, probably to form a plateau. On cooling each system the hydrogen was reabsorbed only in part. Cooling curves showed no breaks below 582° C except in the case of the NaOH-NaH system which gave a small break at 443° C (the M.P. of NaOH is alleged to be 318° C). It is surprising that no break at 318° C or 90° C was found.

III-3-1 Calcium Hydride

The first studies of the Ca-H system given in Progress Report No. 31 are considered to be unreliable, since the pump used in degassing the bombs was subsequently found to be defective. These shells were not properly degassed and may well have been exposed to an oil mist from the pump and mercury vapor. The series was repeated using a prolonged period for degassing at 400° C (which removed small amounts of hydrogen). Dissociation pressures obtained from 99+% CaH₂ and shown in Fig. (21) are in reasonably good agreement with values reported by Johnson⁽²⁸⁾, who employed doubly distilled calcium. Our results are slightly higher, but the "100%" material failed to reabsorb a small part of the evolved hydrogen on cooling. This indicates the effect of some impurity. While traces of nickel were found in opened bombs, other metals are absent. Oxygen, nitrogen, and carbon are present in traces and may have an effect other than that observed when Ca₃N₂ or CaC₂ are added deliberately. The differential heats of formation were calculated from the slopes of Fig. (21) as follows:

$$\Delta H \text{ for CaH}_2 (100\%) = 29.8 \text{ Kcal (Johnson gives 36.75)}$$

$$\Delta H \text{ for CaH}_{1.98} (99\%) = 47.6 \text{ Kcal}$$

Analysis of an opened shell indicated that diffusion losses were negligible; however, the material appears to consist of varicolored particles indicating trace impurities. No melting was observed, although some

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sintering takes place at or below 1000°C . A break occurs at $800\text{--}825^{\circ}\text{C}$ in the cooling curve but is evidently not due to fusion.

III-3-2 Mixtures of Calcium Hydride with CaC_2 and CaF_2

Mixtures were prepared of Baker's C.P. CaC_2 with 99+% CaH_2 in the mol ratio $3\text{CaH}_2:1\text{CaC}_2$ and of Fluorspar crystalline CaF_2 with 99+% CaH_2 in the mol ratio $5\text{CaH}_2:1\text{CaF}_2$. These were loaded (under argon) into stainless steel bombs and degassed at 25°C (3 microns) for 30 mins. On heating the evacuated bombs, dissociation, or at least evolution of gas, occurred. The pressures developed are shown in Figs. (22) and (23). Several per cent of the evolved hydrogen was not reabsorbed on cooling (after curve A was measured). It was bled off and the heating resumed to give curve B. In the case of CaC_2 , the unabsorbed gas, if all hydrogen, represents 3.8% of the original hydrogen present. Once this gas was removed, the system returned to a vacuum on cooling. The CaF_2 system behaved similarly except that only 0.74% of the initial hydrogen was not reabsorbed on cooling after the first run. The shape of curves A and B leads to the supposition that a gas-producing reaction or a dissociation of some labile constituent occurs in the vicinity of $100\text{--}150^{\circ}\text{C}$. Thereafter the pressure increase along curves A and B (Figs. (22) and (23)) is approximately what one would expect from thermal expansion of this gas. As higher temperatures are approached, the calcium hydride starts to dissociate, causing the upward swing. Once the gas due to the assumed impurity is removed, the curves approach pure CaH_2 (dotted line) indicating that the additive is inert. The cooling curve E of Fig. (22) and (23) indicates that some hydrogen has also been removed from the CaH_2 , presumably by bleeding and diffusion. No evidence of fusion was obtained at 1000°C , although both systems showed a very small inflection in the cooling curve at 800°C . The $\text{CaH}_2\text{--CaF}_2$ bomb contained 44.1g. and the $\text{CaH}_2\text{--CaC}_2$ bomb 44.0 g.

III-3-3 Calcium Hydride-Calcium Nitride

Calcium nitride was prepared by passing purified nitrogen over pure calcium. It analyzed 81.2% Ca (81.1% theoretical) and 18.35% N (18.9% theoretical). A mixture of 25.1 g. CaH_2 (99.5%) with 22.1 g. Ca_3N_2 was prepared under argon and placed in a bomb. It was degassed at room temperature. On heating a pressure of 103 cm. developed below 380°C , then was slowly reabsorbed up to 477°C . This would appear to indicate formation of some -NH_2 compound. The system developed a pressure above 800°C . At 820°C the pressure was only 134 cm. and at 930°C , it was 295 cm.

Following this run the system was allowed to absorb 0.484 g. of hydrogen corresponding to an increase of 40% in the hydrogen content. It was then reheated giving curve A of Fig. (24). On cooling the gas was not completely reabsorbed and 0.055 g. (if hydrogen) were removed. Curve B was then obtained, and after removing an additional 0.028 g. of hydrogen, curve C was obtained. Curve D was obtained by cooling slowly from the peak of curve C. The dotted line is a reference curve for pure CaH_2 .

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No melting was observed, although the cooling curves showed minor inflections at 830-860° C.

It should be noted that calcium amide or mixtures of calcium amide with calcium hydride show a higher NH than pure calcium hydride.

III-4-1 Strontium Hydride

A commercial grade prepared by Metal Hydrides Incorporated was used. It analyzed 2.24% H (theoretical 2.24%) and contained 0.54% Ba, 0.52% C, 0.09% N. The strontium analysis was not reliable. This hydride was crushed under argon and loaded into a bomb as usual. The dissociation pressures are recorded in Fig. (25). On cooling after the "100%" run, 1% of the hydrogen was not reabsorbed; hence the upper curve of Fig. (25) may best be denoted as a "99%" curve. Hydrogen was removed to give the three other compositions shown in the figure. As noted above some of the data reported in Progress Report No. 30 are rejected owing to failure of the pump used in degassing. The values reported here are for entirely new runs, which are in excellent agreement with the previous run No. 1.

The differential heat of dissociation was calculated as 29.7 Kcal/mol H_2 for 99% material and as 48.1 Kcal for the 94% composition.

No indication of melting was observed below 1000° C.

III-5-1 Barium Hydride

Barium hydride was prepared from the purest commercial barium metal and found to have the composition 97.4% Ba (theoretical 98.55%); 1.41% H (theoretical 1.45%); N 0.038%. It was loaded into a stainless steel bomb under argon and degassed at 100° C to 1 micron and 10 hrs. at 300° 3 mm. The data agree fairly well with earlier data given in Progress Report No. 31 despite the fact that the earlier bomb may not have been adequately degassed. Fig. (26) gives the best data obtained. The differential heat of formation is 17.6 Kcal/mol H_2 for the composition 97%. No irreversibility was noted. Melting did not occur.

III-6-1 Recommendations

The dissociation studies reported above are probably reliable in that they constitute a study of hydrides and mixtures of ordinary and not extraordinary purity. The entire program was carried out with the idea of providing practical data as quickly as possible and in this respect it has been successful. There are obvious gaps in the work, particularly the lack of reference curves for materials of extreme purity. It is evident that some impurity has caused the anomalous behavior of calcium and of certain mixtures and undoubtedly accounts for the failure of several systems to reabsorb dissociated hydrogen. Repetition of several runs with hydride made in situ from redistilled metals is recommended. It is also desirable to examine microscopically the contents of bombs, especially those containing mixtures.

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The infusibility of several systems is disappointing, although the surprising stability of " Na_2H " and the NaH-NaOH system is worth remarking. It is recommended that these systems be studied further and that a large number of additives, e.g., MgF_2 , BeF_2 , MgCl_2 , CaCl_2 , etc. be tried. Some guidance to such a program is provided by the theory that eutectics are likely only when the ionic radius of the added constituent differs considerably from that of the principal ion. Moreover the analogy of mixed halide systems, e.g., KCl-LiCl , KCl-NaCl , etc. has not been pursued. A study of systems of the type $\text{MH:M}'\text{X}$ is definitely needed, since metathesis may take place forming quaternary systems such as $\text{MH:MX:M}'\text{H:M}'\text{X}$, where X is halide, hydroxide, nitride, carbide, etc

The very interesting $\text{Ca}_3\text{N}_2\text{-CaH}_2$ system requires further study and a preliminary investigation of amide-hydride systems in general appears to offer some promise.

The irreversible dissociation of NaH may be prevented by a suitable catalyst such as NaCl or some hydrogen-carrying metal such as Ti , Ni , Pd , etc. Further the effect of alternate heatings and coolings should be investigated for all promising systems and the attack on the containers ascertained. Dissociation and melting point studies should be extended to higher temperatures and lower hydrogen contents.

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Part IV

Miscellaneous

An apparatus for preparing hydrides via atomic hydrogen was set up for the preparation of magnesium hydride, but owing to a change in emphasis, was never used.

A sample of thorium hydride was prepared having the composition $\text{ThH}_{3.71}$ and a density of 8.2 g./c.c. It was not studied further (Progress Report No. 26, p 4).

A sample of hafnium hydride, HfH_2 , was prepared (not under SC-2026) and its density determined as 10.5 g./c.c. ($N_H = 6.93$).

A zirconium-nickel alloy, prepared by Metal Hydrides Incorporated, was found to contain more hydrogen than pure zirconium by analysis. The N_H of this material was 10.1, whereas pure ZrH_2 has an N_H of only 7.29 (Progress Report No. 31, p 7).

Calcium titanate and TiO were prepared in connection with a study on preparation of TiH_2 , also Li_3N_2 , CeH_3 , UF_4 .

For additional miscellaneous items, see the index to monthly Progress Reports given on the next page.

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Fig 2

Fig 3

Fig 3A

Fig 4

N_H' as a function of P
Ti-H System

Fig 5

Fig 6

Fig 7

Fig 8

Fig 9

N'_H as a function of P
U-H System

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(*) H.I. Schlesinger et al, U.S. Navy Reports

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Fig 13

0220 058

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Fig 16

LiH DISSOCIATION PRESSURE CURVES

from W. C. Johnson, et al

Fig 17

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Fig 18

NaH Dissociation Pressure Curve

○ Keyes, F. G.

□ Herold, Albert

▽ Metal Hydrides Incorporated

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Fig 20

- Run 1 NaH-CaH₂
- Run 2 NaH-CaH₂
- Run 3 NaH-CaH₂
- △ Run 1 NaH-NaOH
- ▲ Run 2 NaH-NaOH
- ▲ Run 3 NaH-NaOH
- Run 1 NaH-NaF
- Run 2 NaH-NaF
- Run 3 NaH-NaF
- ◇ Curve for 100% NaH

DISSOCIATION PRESSURE CURVES FOR NaH MIXTURES

Fig 21

CaH_2 DISSOCIATION PRESSURE CURVES

- 1 Johnson, et al, 100% CaH_2 .
- 2 100% CaH_2 M.H.
- 3 99% CaH_2 M.H.
- 4 Johnson, et al, 85% CaH_2 .
- 5 Pressure curve for undegassed CaH_2 .

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Fig 22

$\text{CaH}_2\text{-CaC}_2$ SYSTEM

- A 19.1 g. of CaC_2 and 24.9 g. of CaH_2 .
- B Residual pressure corresponding to .0459 g. of H_2 and 3.87% of the total H_2 present was removed after Run 1.
- C Ca. 4% of total H_2 lost.
- D Ca. 5% of total H_2 lost.
- E Cooling curve for Run 4.
- F 100% CaH_2 dissociation pressure curve (M.H.)

Fig 23

CaH₂-CaF₂ SYSTEM

A 14 g. of CaF₂ and 30 g. of CaH₂

B .0106 g. of H₂ removed lowering the H₂ composition 0.74%

C Reduction of ca. 3% of total H₂ previous to this run.

D Reduction of ca. 3+% of total H₂ previous to this run.

E Cooling curve for Curve D.

F 100% CaH₂ Dissociation Pressure Curve (M.H.)

Fig 24

CaH₂-Ca₃N₂ SYSTEM

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Fig 25

SrH_2 DISSOCIATION PRESSURE CURVES

- A Ca. 99% SrH_2 .
- B Ca. 97.5% SrH_2 .
- C Ca. 95% SrH_2
- D Ca. 92.3% SrH_2

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