observed dissociation pressures, between $n = 1.8$ and 2.3.

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Rare Earth–Hydrogen Systems. II. Dispersions in Mercury[1]

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Solid hydrides of metals behave differently toward mercury, this behavior depending to some extent on the bonding type. Pulverized lanthanum and cerium hydrides were found to be wet by mercury, forming dispersions with a strong tendency to adhere to glass. Cerium hydride dispersions decomposed into hydrogen and cerium amalgams above approximately 115° and reacted vigorously with water at room temperature. On exposure to air, dilute dispersions oxidized to cerium(IV) oxide, while the more concentrated preparations oxidized, in part, and precipitated the unchanged hydride, in part. Lanthanum and ytterbium hydride dispersions in mercury yielded X-ray diffraction patterns different from those of the pure hydrides, showing surface formation of new compounds. Uranium hydride in mercury gave the normal diffraction pattern of UH_3. Freezing and melting curves of uranium hydride and cerium hydride dispersions showed no depression of the freezing point of the mercury. Filtration of cerium hydride dispersions through sintered glass removed nearly all of the dispersed phase and gave a filtrate 0.008% in cerium hydride.

Introduction

The behavior of hydrides toward mercury is varied and may afford a probe into their constitution. Lithium hydride, an ionic compound, was treated with mercury by Moers,[2] who observed the evolution of hydrogen and the formation of lithium amalgam. The reaction is slow at the boiling point of mercury, and there is no particular interaction at room temperature. In ammonium amalgams[3] and in the more stable tetramethylammonium amalgams,[4] the freezing point of mercury is depressed, showing that they are true solutions. There is also a large decrease in the interfacial tension of mercury upon incorporation of ammonium radicals.[5] Oxley,[6] on the basis of investigations of the magnetic susceptibility of the palladium–hydrogen system, recognized a similarity in electronic structure between a metal containing hydrogen in a 1:1 atomic ratio and the metal of one higher atomic number. This hypothesis was extended by Ubbelohde,[7] who considered that the bonding in a metal hydride MH_n is, with regard to further metallic bonding, approximately like that of the atom whose atomic number is n higher than that of M. Thus NH_4 and OH_3 amalgams are expected to resemble Na amalgams, and PdH is expected to resemble Ag.

Uranium hydride is a compound manifesting metallic character, even though metal–metal bonding is unimportant in its structure.[8] Warf, *et al.*,[9] found that it forms pseudo-amalgams; *i.e.*, the hydride surface is tenaciously wet by mercury, apparently through metallic bonding. The preparations are evidently not true solutions, but dispersions ranging from solids through gels to liquids, depending on concentration. The treatment of uranium hydride with mercury depresses the mercury–glass interfacial tension, as strong adherence to the glass is noted, forming mirrors. There is no heat effect, in contrast to amalgamation of finely divided uranium, which reacts to form intermetallic compounds. Other metals also wet uranium hydride.

Paal and Steyer[10] showed that mercury extracts aqueous colloidal palladium hydride. Ubbelohde[7] found that palladium hydride ($PdH_{0.6}$) is wet rapidly by mercury, evolving considerable heat and some hydrogen. Both palladium amalgam ($PdHg_{5.2}$) and the hydride amalgam ($PdH_{0.15}Hg_4$) are diamagnetic, suggesting that the d orbitals of palladium are saturated. Mercury was found to wet palladium, iron, and platinum after these metals, immersed in aqueous solutions, were connected to a cathode; this was ascribed to the formation of metallic bonds between the mercury atoms and the surface hydride groups, produced by electrolysis.

There is no mention of the interaction of the hydrides of the rare earth metals with mercury in the chemical literature. The metallic character of these hydrides

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would lead one to anticipate a behavior toward mercury resembling that of uranium hydride or palladium hydride.

Experimental Procedures and Results

Materials.—The rare earth metals and hydrogen are described in the preceding paper. The mercury employed was of analytical reagent grade.

Treatment of Rare Earth Hydrides with Mercury.—Lanthanum hydride (LaH_3) or cerium hydride ($CeH_{2.7}$) was prepared in one arm of an inverted V-shaped tube, which also contained a polished glass rod. The other arm contained mercury. Agitation of the apparatus in an eccentric shaker, with the glass rod serving as a hammer, reduced the hydride to a black powder. When the mercury was poured over onto the hydride, instant wetting occurred, to form a viscous mass which adhered to the glass as a mirror. No heat effect was noted. Preparations ranged from 5 to 35% hydride.

Thermal Stability of Cerium Hydride in Mercury.—A 5.1% cerium hydride dispersion in mercury attached to the vacuum system was heated in a bath. It was found that the first noticeable hydrogen was evolved at 115–120° and that at 200° hydrogen was being expelled rapidly. Mercury–cerium intermetallic compounds were evidently formed.

Reaction of Cerium Hydride in Mercury with Air and with Water.—Concentrated mixtures of cerium hydride and mercury, on exposure to air, rapidly developed voluminous black precipitates and invariably ignited spontaneously within a few minutes. A portion of the black precipitate, prepared with limited air, was quickly withdrawn before ignition and sealed in a capillary. Its X-ray diffraction pattern showed it to be reasonably pure cerium hydride. It would appear that formation of an oxide layer on the hydride particles resulted in the separation of the particles from the mercury, disrupting the dispersion. The behavior of uranium hydride dispersions is parallel.

On admission of air to the more dilute preparations, a thin layer of yellowish green scum formed over the shiny surface. A portion of this scum, by X-ray analysis, was identified as cerium dioxide of poor crystallinity or small particle size (diffuse lines). Ignition of the yellowish material gave a white product which corresponded to highly crystalline cerium dioxide (sharp diffraction lines).

One bulb of cerium hydride in mercury (4.8% hydride) was broken under water. A vigorous reaction ensued, with abundant evolution of hydrogen and considerable sparking. It should be noted that uranium hydride in mercury is relatively inert toward water.

Mercury Dispersions of Ytterbium Hydride.—Some ytterbium metal was converted to the dihydride, and this was powdered under vacuum as in the case of cerium hydride. Admission of mercury formed a dispersion at once, which precipitated the hydride on contact with air.

X-Ray Diffraction Patterns of Hydrides in Mercury.—The tip of an evacuated capillary containing $LaH_{1.99}$ was broken under mercury, and then resealed with cement. X-Ray diffraction patterns were made both immediately after sample preparation and again 60 days later. The patterns were similar, but the lines of the later pattern were much sharper. The lines did not match those of lanthanum, lanthanum hydride, or any of the four lanthanum–mercury compounds reported by Iandelli and Ferro.[11] Unfortunately, we were unable to index the pattern and determine the unit cell.

The interaction of lanthanum hydride with mercury was further investigated with the use of an apparatus (Figure 1) in which the hydride could absorb mercury vapor at room temperature. A drop of mercury was introduced into the bulb but was not allowed to flow onto the hydride. The first X-ray exposure showed only the pattern of lanthanum hydride, but after 18 days, the pattern of the La–H–Hg material could be detected. With the passage of time, periodic X-ray exposures showed that the former pattern gradually disappeared, and only the latter could be seen after 130 days.

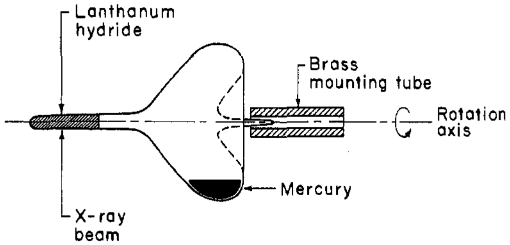

Figure 1.—Apparatus for absorption of mercury vapor by lanthanum hydride.

An X-ray diffraction pattern of ytterbium hydride dispersed in mercury did not show the lines of YbH_2 but showed a new set of lines, which could not be interpreted.

Finally, a capillary of uranium hydride was broken under mercury to form the dispersion and an X-ray pattern made. In this pattern only the normal lines of UH_3 appeared.

Freezing and Melting Curves of Hydrides in Mercury.—While previous work had suggested that the hydrides in mercury were dispersions rather than true solutions, it was still conceivable that a small fraction dissolved to form a genuine amalgam. The rather high molal freezing point depression constant of mercury (39.4°, based on a heat of fusion of 2.34 kjoules/g-atom)[12] affords a sensitive means of testing this point by detecting any freezing point depression.

A melting and freezing apparatus was constructed which was attached to the vacuum line for preparation of the hydride and its dispersion in mercury. After sealing off, it was immersed in a small dewar flask inside a larger one, and both flasks were filled with a Dry Ice–trichloroethylene mixture. Temperatures were measured using three-element copper–constantan thermopiles and were precise to 0.03°. The specimens were agitated violently during the warming or cooling periods.

Freezing curves of pure mercury showed strong supercooling despite violent agitation. The plateaus of both freezing and melting curves were found at $-38.84 \pm 0.03°$, in satisfactory agreement with the very accurate value of $-38.87°$ determined by Smits and Muller.[13] A viscous 30.3% dispersion of uranium hydride in mercury, which adhered strongly to the glass, showed plateaus at $-38.86 \pm 0.03°$, within experimental error of the melting point of pure mercury. Melting and freezing curves of a 5.1% dispersion of cerium hydride ($CeH_{2.7}$) showed plateaus at $-38.83 \pm 0.03°$. Some supercooling was observed in the freezing runs, after which the temperature rose rapidly to the plateau level.

The evidence in the cases of uranium hydride and cerium hydride dispersions is that they are not true solutions or amalgams, but dispersions. With the sensitivity limit of 0.03° in the temperature-measuring apparatus, and thus a maximum freezing point depression of 0.03°, the true solubility of the hydrides in mercury cannot be more than approximately 0.0007 *M* at the freezing point, corresponding in the case of cerium hydride to 0.01%.

Filtration of Mercury Dispersion of Cerium Hydride.—A specimen of cerium hydride was comminuted by the eccentric drive-hammer technique, and mercury was added to form a 5.5% dispersion. The stiff preparation was shaken down into a side arm with a "fine" sintered-glass filtering disk. This side arm was torched off and centrifuged, leaving a thick, nearly solid residue on the disk. The residue was a concentrated dispersion, while the filtrate had the appearance of pure mercury. The filtrate was found by analysis to contain 0.0079% cerium hydride.

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Discussion

Ready wetting and dispersion of rare earth hydrides by mercury verifies their metallic character. In that there is little or no heat effect on dispersion, they resemble uranium hydride rather than palladium hydride. The difference in density between mercury (13.6 g/cc) and LaH_3 (5.35 g/cc) or $CeH_{2.7}$ (5.55 g/cc) is considerably greater than in the case of mercury and UH_3 (10.9 g/cc), a factor apparently unimportant in the dispersion process. The wetting and dispersion by mercury of orthorhombic YbH_2, a manifestation of metallicity, is in conformity with the conducting and magnetic properties of this compound.[14] The breaking of the dispersions on exposure to air evidently results from formation of oxide films which invade the hydride–mercury boundary of each particle.

The nature of the interaction of the lanthanide hydrides with mercury remains obscure, but it is certain that new compounds, evidently ternary compounds (R–H–Hg), are formed. Since air breaks the dispersions and precipitates the hydrides, it is probable that the new compounds are formed only on the surface of the hydride particles.

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Rare Earth–Hydrogen Systems. III. High-Pressure Investigations[1]

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A steel high-pressure line that permitted the measurement of pressures up to 65 atm was built and the hydrides of La, Ce, and Yb were investigated. From the equilibrium *P–T–C* data obtained, lines of constant composition (isosteres) were plotted. From the slopes of these lines, approximate enthalpy values were obtained for the reaction $RH_{3-x} = RH_{2-y} + [(1 + y - x)/2]H_2$. Partial molal heats of dissociation of $LaH_{2.70}$ and $LaH_{2.80}$ are 18.9 and 17.0 kcal/mole of H_2, respectively, while those for $CeH_{2.80}$ and $CeH_{2.90}$ are 16.3 and 15.6 kcal/mole of H_2, respectively. The lattice constant for $CeH_{2.97}$ was determined to be 5.539 ± 0.001 A. It was found possible to synthesize a new, higher hydride of ytterbium, an fcc substance resulting from additional absorption of hydrogen by the orthorhombic dihydride. Isotherms for the region $1.9 < H:Yb < 2.6$ below approximately 13 atm and 320° contained plateaus which indicate a two-solid-phase equilibrium (YbH_2 and $YbH_{2.55}$), while above these critical conditions only one solid phase exists. From a van't Hoff plot of the plateau pressures *vs.* reciprocal absolute temperature, the value for ΔH_{diss} of $YbH_{2.55}$ to YbH_2 was calculated to be 6.6 kcal/mole of H_2. Attempts to prepare higher hydrides of Eu and Sc by the reaction of the metals with hydrogen at elevated temperatures and pressures were unsuccessful.

Introduction

We have extended pressure–temperature–composition measurements of the rare earth–hydrogen systems into the region of high dissociation pressure (where H:R approaches 3). The investigations of the europium- and ytterbium–hydrogen systems were of particular concern because it seemed likely that the predicted thermodynamic stability of trihydride phases placed them within range of attainable high pressures. Unlike the rest of the rare earth metals, europium and ytterbium absorb hydrogen at less than 1 atm pressure to form only the dihydrides,[2] which have orthorhombic structures like the hydrides of the alkaline earth metals. Two preliminary accounts of the high-pressure work have been published.[3,4]

To study the rare earth–hydrogen systems where their dissociation pressures are greater than 1 atm, a stainless steel high-pressure system was built. The high-pressure line was similar to those used by Gibb, *et al.*,[5] and by Libowitz and Gibb[6] in their studies of the titanium–hydrogen and uranium–hydrogen systems; however, since the apparatus developed for this work contained several important modifications, it will be described in some detail.

Experimental Section

Apparatus.—The apparatus consisted of a high-vacuum system connected to the high-pressure line, schematically shown in Figure 1. This consisted originally of two $^5/_8 \times 2^1/_4$ in. stainless steel bombs, one of which contained the sample and the other uranium hydride with which to pressure the system. The sample bomb held a 1000 psi Ashcroft laboratory test gauge (graduated in 5-psi divisions) which had been calibrated against a dead-weight gauge. Steel tubing ($^1/_4$-in. o.d. by $^1/_{16}$-in. i.d.) and several

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