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.

Acknowledgments.—This work was supported in part by the Office of Naval Research (Contract Nonr 22815). W. L. K. acknowledges with thanks the grant of a U. S. Atomic Energy Commission predoctoral fellowship, 1951–1953.

[14] J. C. Warf and K. I. Hardcastle, *Inorg. Chem.*, **5**, 1736 (1966).

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

BY KENNETH I. HARDCASTLE AND JAMES C. WARF

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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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[1] Based in part on the Ph.D. dissertation of K. I. Hardcastle, University of Southern California, Aug 1961.

[2] W. L. Korst and J. C. Warf, *Acta Cryst.*, **9**, 452 (1956).

[3] J. C. Warf and K. I. Hardcastle, *J. Am. Chem. Soc.*, **83**, 2206 (1961).

[4] J. C. Warf and K. I. Hardcastle in "Rare Earth Research," J. F. Nachman and C. E. Lundin, Ed., Gordon and Breach Science Publishers, New York, N. Y., 1962, pp 261–271.

[5] T. R. P. Gibb, Jr., J. J. McSharry, and R. W. Bragdon, *J. Am. Chem. Soc.*, **73**, 1751 (1951).

[6] G. G. Libowitz and T. R. P. Gibb, Jr., *J. Phys. Chem.*, **61**, 793 (1957).

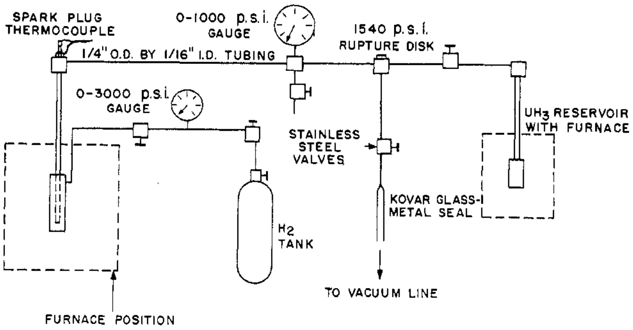

Figure 1.—Schematic diagram of the steel high-pressure line.

Aminco stainless steel needle valves and fittings were employed. The bombs were prepared by atomic hydrogen welding the separate parts together which were machined from Type 347 stainless steel rod and a length of $^{3}/_{16}$-in. i.d. Type 347 stainless steel tubing. Leak-free connections between the various components were obtained by compressing the steel tubing or bomb tubes, which were tapered at a 59° angle at their ends, into the stainless steel fittings whose seats were cut at a 60° angle. The Aminco stainless steel "tees," elbows, couplings, rupture-disk tee (adjustable bursting pressure 1500–15,000 psi), and valves were all rated to withstand a minimum pressure of 15,000 psi. The furnace used to maintain the sample temperature was the one constructed and used in the studies of the rare earth–hydrogen systems at low pressure.[7]

Early experiments on the lanthanum–hydrogen and cerium–hydrogen systems pointed out two areas in the high-pressure line which needed improvement. One, the loss of hydrogen from the system by diffusion through the walls of the sample bomb at the elevated temperatures, was expected from the work of Gibb, *et al.*[5,6] The other was the large thermal gradient between the temperature recorded outside the bomb and the actual sample temperature within.

The loss of hydrogen from the system was a serious problem in that it vitiated the subsequent hydrogen balance calculations unless an accurate estimate of the amount of hydrogen which diffused out could be made. To prevent any loss of hydrogen by diffusion from the hot bomb, a simple but extremely effective bomb, shown in Figure 2, was designed. The pressure in the inner bomb was balanced by an equal or slightly greater hydrogen pressure in the outer bomb. This outer section was connected by means of similar high-pressure fittings to a 0–3000 psi pressure gauge and through a valve to a cylinder containing hydrogen at a pressure of 900 psi. Hydrogen from this cylinder was admitted to the outer bomb system as often as was necessary to compensate for diffusion of hydrogen through the walls of the outer bomb at the elevated temperatures.

Since the addition of the outer bomb further increased the thermal gradient between the outside and inside, the temperature of the sample itself was measured using an internal thermocouple. An ordinary automobile spark plug (AC brand, M-8 type, 10 mm) with a lead gasket was used to connect the thermocouple. The $^{3}/_{8} \times ^{3}/_{8}$ in. stainless steel elbow to which the sample bomb was connected was drilled and tapped opposite the bomb hole to receive the spark plug. The chromel–alumel thermocouple was hard-soldered to the spark plug so that the chromel wire was connected through the center insulated electrode while the alumel wire was connected through the base. The wires inside the bomb were protected by enclosing them in porcelain thermocouple insulators so that only the hot junction at the end of the insulators was exposed. The high-pressure line thus assembled did not leak perceptibly, even when subjected to hydrogen pressures of the order of 40–50 atm for prolonged periods at elevated temperatures. Additional thermocouples were positioned on the outside of the sample bomb to record the various temperature gradients. The thermocouples were calibrated before and after the experiments on each rare earth–hydrogen system using standard melting-point samples of NBS zinc and aluminum and pure silver. The reliability of the spark plug thermocouple was critically examined to observe any effect from the junction potentials present owing to its construction, and none could be found. Initially, the thermocouples were accurate to within 0.05% of the correct temperature; however, they were observed to deviate at the end of an experiment by as much as 0.1–0.5%.

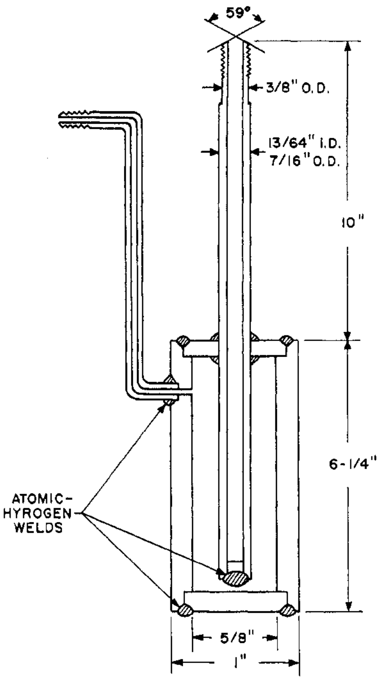

Figure 2.—Double-walled bomb.

For the cerium–hydrogen high-pressure experiments the chromel–alumel spark plug thermocouple was replaced by a platinum—platinum–13% rhodium thermocouple. This was necessary since examination of the chromel–alumel thermocouple after the initial ytterbium–hydrogen experiments showed that it had been attacked slightly. Thermocouple voltages were measured with a Leeds and Northrup portable precision potentiometer, Model No. 8662.

Materials.—The rare earth metals used were generally of the highest purity available. The lanthanum and cerium were obtained from Dr. F. H. Spedding, as already described.[7] The europium metal was courteously prepared by Dr. Adrian Daane at Iowa State University by reduction of the oxide with lanthanum and simultaneous volatilization, according to the method used in the preparation of samarium and ytterbium metals described by Daane, Dennison, and Spedding.[8] The europium oxide was prepared from europium oxalate decahydrate which was kindly loaned to us by Mrs. Herbert N. McCoy. The metal contained 150 ppm of La or Ca, with Gd, Sm, Fe, Cu, Ta, and Si not detected.[9] The ytterbium metal was purchased from Research Chemicals, Burbank, Calif., and was reported to contain the following maximum amounts of impurities: 0.1% O and Lu, 0.03% Fe and Ca, 0.01% Mg. The scandium metal was prepared by Dr. F. H. Spedding's group by reduction of the fluoride with calcium metal. The fluoride was prepared in this laboratory by heating together a mixture of 2 g of 99.9% Sc_2O_3 purchased from Research Chemicals, Burbank, Calif., with approximately 3 g of NH_4HF_2 in a platinum dish. The ScF_3 was then outgassed by heating in a Vycor tube to 800° *in vacuo.*

Samples of the rare earth metals were obtained by cutting pieces of the desired size and shape from the massive ingots. In

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(7) W. L. Korst and J. C. Warf, *Inorg. Chem.*, **5**, 1719 (1966).

(8) A. H. Daane, D. H. Dennison, and F. H. Spedding, *J. Am. Chem. Soc.*, **75**, 2272 (1953).

(9) F. J. Spedding, private communication, 1955.

almost all instances the final cleaning and weighing of the samples were carried out while the metal was protected with a dry, protective atmosphere (either N_2 or CO_2), using a glove box. The metal was then transferred to the apparatus and the vessel quickly evacuated to approximately 10^{-5} mm.

Tank hydrogen was passed through a Deoxo platinized catalyst unit to convert the oxygen impurity to water, then through a drying tube containing Anhydrone, and finally through a Vycor reservoir containing uranium–uranium hydride at approximately 700° to remove any last traces of oxygen. Sometimes the hydrogen was obtained by thermal decomposition of the uranium hydride in the reservoir.

Preparation of the Hydrides.—The metal in the evacuated apparatus, either the high-pressure sample bomb or a Pyrex vessel, was outgassed by heating for a short period of time at 250–350° and was usually allowed to cool before the hydrogen was admitted. Purified hydrogen gas from the storage bulbs or from the uranium hydride reservoir was let into a calibrated portion of the vacuum line, and after thermal equilibrium was established, the pressure and temperature were noted. The hydrogen was admitted into the evacuated apparatus containing the metal sample, which was then heated to approximately 350° and maintained at this temperature for several hours to ensure maximum absorption and homogenization of the sample. The vessel was then slowly cooled to room temperature, and the composition of the hydride was ascertained by calculation.

Pressure–Temperature–Composition Measurements.—To obtain dissociation pressure data at high pressures, the rare earth hydride sample at room temperature was subjected to various external pressures of hydrogen and then heated until its dissociation pressure was greater than the initially imposed pressure. With each metal–hydrogen system studied, some of the data were obtained isothermally. That is, the sample was maintained at a constant temperature, and a measured portion of the hydrogen was removed from the gas phase of the high-pressure system to the vacuum line. After the new equilibrium was established, the pressure was recorded.

In each experimental run the typical procedure was as follows. The rare earth metal (5–10 g), in the sample bomb with temperature-controlled furnace positioned around it, was hydrided as previously described. Hydrogen was admitted to the high-pressure portion of the line from the uranium hydride reservoir to the desired pressure and then isolated by closing the valve. This step was always carried out with the specimen at room temperature so as to avoid sorption of hydrogen by the sample at this time, and no significant sorption of hydrogen was observed in any experiment. When the system had reached thermal equilibrium, the pressure and temperature were recorded so that the number of moles of hydrogen initially present in the gas phase could be calculated. The temperature-controlled furnace was operated, and after equilibrium had been established at the desired temperature, the pressure was noted. These temperatures were, in the experiments on the lanthanum–hydrogen system using the single-walled bomb, the temperature of the sample in the bottom portion of the bomb and the temperature (room) of the remainder of the high-pressure line. In the experiments on the cerium– and ytterbium–hydrogen systems using the double-walled sample bomb, an additional temperature was recorded, namely, in the gradient region of the bomb stem inside the furnace between the hot, double-walled region containing the specimen and the relatively cool remainder of the system outside the furnace. The hydride was thus heated and the temperature was arrested periodically for the pressure–temperature measurements until the desired maximum temperature (500–700°) was reached, when the sample was cooled to room temperature. Several equilibrium pressures and temperatures were also measured during the cooling cycles to check the systems for hysteresis. Apparent hysteresis was observed in several experimental runs; however, the explanation was not hysteresis, but the fact that there had been leakage from the system or further absorption of hydrogen by the sample. It was observed that equilibrium was more slowly achieved in a cooling or absorption run than in a heating or dissociation run. Also, equilibrium was attained much more slowly at the lower temperature (<250°).

The volume of the high-pressure line, determined by expansion of carbon dioxide and of hydrogen from the calibrated section of the vacuum line into the single-walled bomb, was 55.4 cc and with the double-walled sample bomb it was 27.2 cc. The volumes of hydrogen in the hot and gradient regions of the sample bombs were determined by calculation from the dimensions of the bomb as well as by measurement with water. The thermal expansion of the sample bombs was considered, and calculations showed that this could be neglected in the case of the double-walled bomb (<0.5%). However, the change in volume of the single-walled bomb with increasing temperature was quite significant and was taken into account in the calculations on the lanthanum–hydrogen system. Somewhat arbitrarily, equilibrium was considered to be established when the pressure and temperature did not vary by more than 0.5% of their respective values during the period of 0.5–1 hr. The reproducibility of the dissociation pressure data during reabsorption of the hydrogen by the sample was additional evidence for the supposition that the measured pressures represented true equilibrium values; that is, equilibrium could be approached from above or from below.

Calculation of the composition of the solid hydride for any set of equilibrium data was carried out using the original measurements as well as additional values obtained from a smooth curve drawn through a plot of the P–T data. It is obvious that hydrogen which is lost by either diffusion or leakage from the high-pressure line is counted as hydrogen absorbed by the sample. Therefore, either accurate evaluation of the leakage (diffusion) rate under various conditions or a leak-proof apparatus is necessary before one can confidently calculate the composition of the solid. The analysis of the hydride after the experimental runs gave the final composition.

Corrections for the nonideality of hydrogen at these pressures were made using the tabulated values[10] for the compressibility factor, z, where $z = PV/nRT$. With each of the systems studied the initial high-pressure run was at 30–50 atm. This was to permit any additional absorption of hydrogen to take place, inasmuch as the hydrides were prepared at low pressures (<1 atm). The final experimental run with each system was also at relatively high pressures, and the sample was slowly cooled to allow maximum absorption of hydrogen by the solid.

Several blank experiments on the high-pressure system containing only hydrogen were performed to check diffusion losses and the reliability of the calculation of the amount of gas present in the line at any pressure and temperature. A known amount of hydrogen was heated, several arrests of the temperature were made, and the corresponding pressures were recorded. It was found that it was possible to determine the number of moles of hydrogen to within 1–2% using the single-walled bomb and to within approximately 0.5% with the double-walled bomb.

The pressures were measured to ±0.5 psi and the temperatures to 1–2° as previously stated. These, along with the measurements of the system containing only hydrogen, suggest errors of approximately 1% in the composition (±0.03 H:La units) in the lanthanum–hydrogen system calculations and 0.2–0.5% in composition (±0.02 H:Ce and H:Yb units) in the cerium– and ytterbium–hydrogen system calculations.

X-Ray Diffraction Studies.—The general techniques described earlier[7] were followed. The values of θ were always corrected for film shrinkage, which amounted to 0.1–0.3%. In general, the data were also corrected for absorption by plotting the values of the lattice constant calculated for each value of θ against the Nelson–Riley[11] or Taylor–Sinclair[12] function. The least-squares line for the linear function was computed, and the standard de-

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[10] National Bureau of Standards, Circular 564, "Tables of Thermal Properties of Gases," U. S. Department of Commerce, National Bureau of Standards, U. S. Government Printing Office, Washington, D. C., 1955.

[11] J. B. Nelson and D. P. Riley, *Proc. Phys. Soc.* (London), **57**, 160 (1945).

[12] A. Taylor and H. Sinclair, *ibid.*, **57**, 123 (1945).

viation was obtained. This treatment corrected for essentially all but the systematic errors. No temperature corrections were made, but the sample temperatures were approximately 22° at all times.

Results and Discussion

Lanthanum–Hydrogen.—Lanthanum in the single-walled bomb was converted to $LaH_{2.87}$. Plots of the dissociation pressure data obtained for the different initial pressures are presented in Figure 3. The curves clearly consist of two sections: A, which shows the pressure increase due to thermal expansion of the hydrogen, and B, which represents the thermal dissociation of the hydrogen-rich lanthanum hydride. Region B can be described by the general equation

$$RH_{3-x} \longrightarrow RH_{2-y} + \frac{1+y-x}{2}H_2 \qquad (1)$$

where x and y are variables and are small and primarily dependent upon the temperature and pressure.

The calculated data are plotted in Figure 4 (in the form $\log P = Dn - E$), along with the data for a 606° isotherm obtained earlier.[7] The number of points plotted in Figure 4 is small owing to the relatively few reliable dissociation runs obtained using the single-walled bomb. Many runs were discarded because of known or suspected leakage of hydrogen either by diffusion through the hot walls of the sample bomb or by leakage at the connections.

The good agreement between the 606° isotherm as extended by the dashed line in Figure 4 and the results of this investigation may be fortuitous, since this agreement was not experienced in the more rigorously and more carefully examined cerium–hydrogen system.

Cerium–Hydrogen.—The low-pressure reaction of cerium metal with hydrogen in the double-walled bomb resulted in a sample with the composition $CeH_{2.89\pm0.01}$. The line was pressured to approximately 30 atm, and the sample was heated to 300–400° for several days. Calculations of the additional moles of hydrogen absorbed by the sample from the pressure decrease gave the formula $CeH_{2.95\pm0.01}$. During the course of the experimental decomposition runs, slight additional absorption of hydrogen was also observed. Calculation of the composition of the hydride at the end of the dissociation pressure measurements gave $CeH_{2.98\pm0.03}$.

Analysis of the black, extremely pyrophoric cerium hydride for hydrogen after completion of the runs gave the composition as $CeH_{2.97\pm0.06}$. The hydride was decomposed with acid and the amount of hydrogen evolved was measured, using a modified Dumas apparatus.[13] During subsequent analyses to improve upon the precision given above, it was noticed that excess pressure in the sample storage tube had loosened the waxed, ground-glass cap. All subsequent analyses of this material for hydrogen by various methods showed the composition to be $CeH_{2.6}$–$CeH_{2.7}$. A portion of this sample kept in an evacuated tube for 1 week (25–30°) released roughly 10% of its hydrogen. Since the hydrogen-rich rare earth hydrides (H:R approximately 3) are extremely reactive, it was suspected that perhaps the $CeH_{2.97}$ had reacted with the drybox atmosphere, nitrogen. A semimicro Kjeldahl analysis of the solution from the hydrogen determination was performed, but no detectable nitrogen was present.

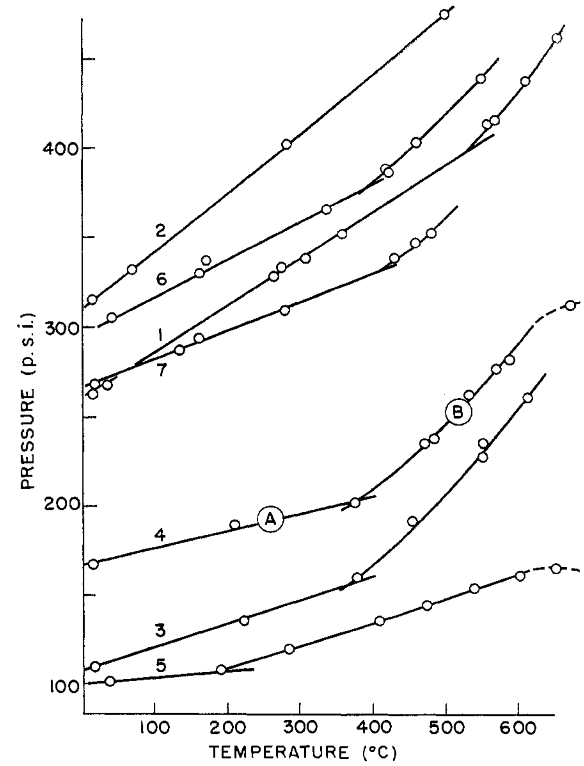

Figure 3.—Experimental data for the lanthanum–hydrogen system at high pressures.

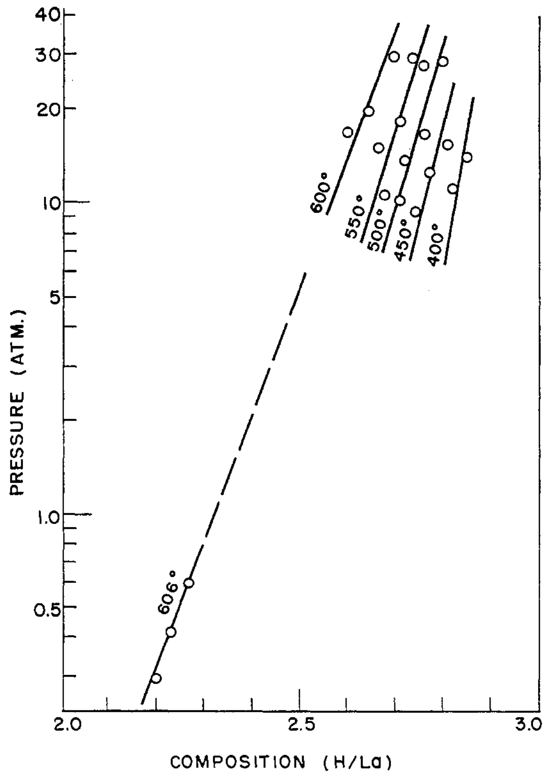

Figure 4.—Isotherms for the lanthanum–hydrogen system.

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[13] J. C. Warf and K. I. Hardcastle, *Inorg. Chem.*, **5**, 1736 (1966).

Cerium trihydride evidently slowly decomposes to $CeH_{2.7}$ at room temperature (*vide infra*).

Figure 5 shows plots of the data obtained from the cerium hydride dissociation experiments. The calculated P–T–C data are plotted in Figure 6, along with other low- and high-pressure results from various authors. The experimental dissociation results are for the region $2.3 < H:Ce < 3$, and at no time during the runs were the plateau regions involved. The isotherms show that extremely high pressures are necessary to inhibit the dissociation of hydrogen-rich cerium hydride at temperatures much above room temperature. The correlation between the high-pressure results of this investigation and the low-pressure results[7] is not satisfying. The high-pressure curves of Streck and Dialer[14] do appear to be in fair agreement with the low-pressure results at the lower temperatures, but at higher temperatures correspondence is poor. The results of Streck and Dialer are presented as only a few points in Figure 2 in their publication on the cerium–hydrogen system, and these extend the low-pressure isotherms (300–600°) to approximately 60 atm. There was, however, no mention whatsoever of these data in the text and they cannot be critically evaluated.

It is difficult to decide upon the reasons for the observed disagreement in results. Temperature gradients are always present in these studies and attempts to consider them are usually made. It is also possible, since the hydride compositions are generally calculated on the basis of the weighed sample only, that as little as 0.5% unreacted cerium (or oxide) could displace the composition abscissa 0.02 unit and could possibly account for the observed discrepancies.

The compositions calculated in these experiments are only on the basis of the weight of the specimen used. Thus, taking into account the purity of the cerium metal used for the experiments, the hydride can be considered as being essentially stoichiometric CeH_3 containing a small amount of impurities. We feel that previous investigators attempting to prepare the stoichiometric hydrides of the rare earths as well as of other metals did not sufficiently consider this when discussing their results, *e.g.*, $CeH_{3.000 \pm 0.002}$.[15] An example of taking these considerations into account is presented by Spedding, *et al.*,[16] in their study of the uranium–hydrogen system.

Lines of constant composition (isosteres) are plotted in Figure 7 from the isotherms of Figures 4 and 6. The slopes of the curves corresponding to B in the equation

$$\log P_{\text{atm}} = A - \frac{B}{T} \qquad (2)$$

were determined and are listed in Table I. Thus it is possible to evaluate approximately the partial molal heat of dissociation, ΔH_{diss}, for reaction 1 using the values of B obtained above and the equation

$$\frac{d(\log P_{\text{atm}}{}^{n})}{d(1/T)} = -\frac{\Delta H_{\text{diss}}}{2.303R},\; n = \frac{1 + y - x}{2} \qquad (3)$$

where n is the number of moles of hydrogen produced by the dissociation of 1 mole of compound RH_{3-x}. Integration of the above equation yields

$$\log P = \frac{\Delta H_{\text{diss}}}{2.303nRT} + \text{constant} \qquad (4)$$

which is equivalent to expression 2 describing the experimental relation between the pressure and temperature. Strictly, the van't Hoff isochore is applicable only to the plateau pressure regions where the hydrogen-poor phase is being converted to the hydrogen-rich phase. However, extension of this equation to permit estimation of ΔH_{diss} for the solid solution or hydrogen-rich region appears justifiable since the isosteres are linear over a large temperature range. The heats of dissociation are also given in Table I.

TABLE I
PARTIAL MOLAL HEATS OF DISSOCIATION FOR HYDROGEN-RICH LANTHANUM AND CERIUM HYDRIDES

R	H:R	B	ΔH_{diss}, kcal/mole of H_2
La	2.80	3700	17.0 ± 0.7
La	2.70	4100	18.9 ± 0.7
Ce	2.93	2950	13.0 ± 2.0
Ce	2.90	3300	15.6 ± 0.7
Ce	2.80	3530	16.3 ± 0.5
Ce	2.70	3750	17.1 ± 0.5
Ce	2.60	4360	20.0 ± 1.0
Ce	2.50	5210	22.0 ± 1.0

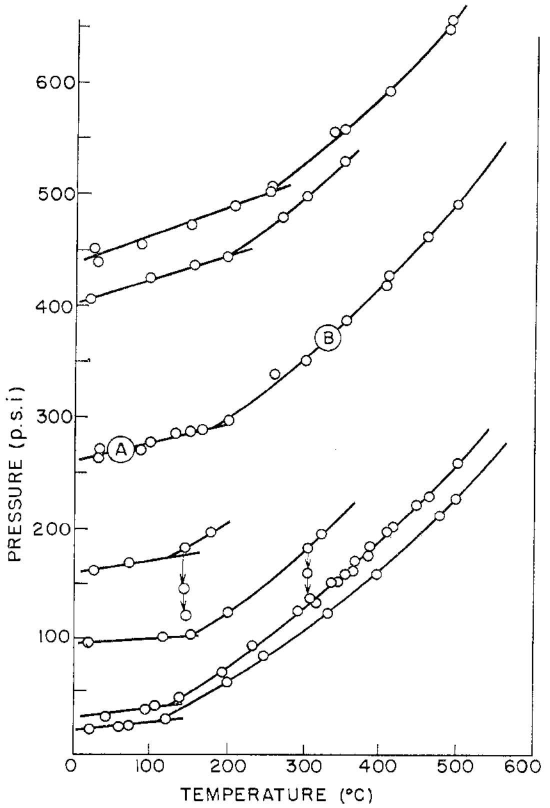

Figure 5.—Experimental data for the cerium–hydrogen system at high pressures.

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[14] R. Streck and K. Dialer, *Z. Anorg. Allgem. Chem.*, **306**, 141 (1960).

[15] K. Dialer and W. Rothe, *Naturwissenschaften*, **42**, 44 (1955).

[16] F. H. Spedding, A. S. Newton, J. C. Warf, O. Johnson, R. W. Nottorf, I. B. Johns, and A. H. Daane, *Nucleonics*, **4**, No. 1, 4 (1949).

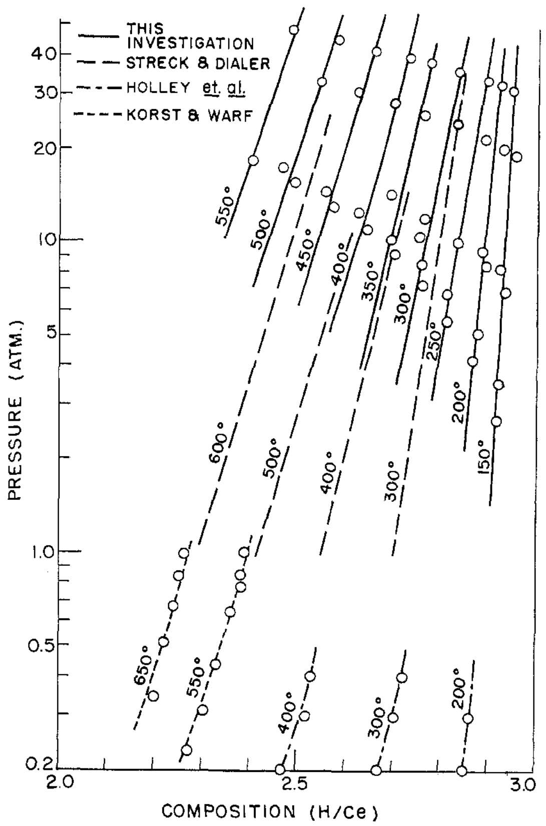

Figure 6.—Isotherms for the cerium–hydrogen system.

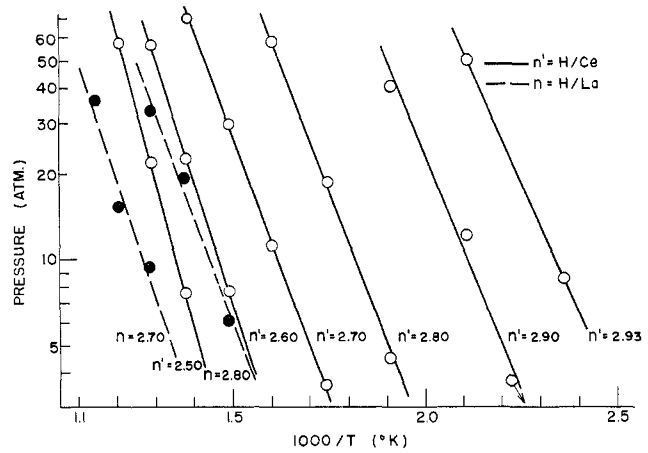

Figure 7.—Log *P vs.* reciprocal temperature curves for constant compositions, La–H and Ce–H systems.

The values obtained for ΔH_{diss} can be favorably compared with the 17 kcal/mole of H_2 predicted by Streck and Dialer,[14] the dissociation process being described as two separate steps

$$2CeH_3 \longrightarrow 2CeH_2 + H_2 \quad \Delta H_{diss} = +15 \text{ kcal/mole of } H_2$$

$$CeH_2 \longrightarrow Ce + H_2 \quad \Delta H_{diss} = +49 \text{ kcal/mole of } H_2$$

One can estimate from the experimentally determined equation relating the equilibrium dissociation pressure with temperature what would be the approximate ambient dissociation pressure of $CeH_{2.93}$. The relation $\log P_{atm} = -2950/T + 7.92$ gives roughly 9 mm at 27°, while a similar calculation for $CeH_{2.90}$ gives 1 mm. The expected dissociation pressure for $CeH_{2.97}$ would then be considerably higher and would explain loss of hydrogen at room temperature.

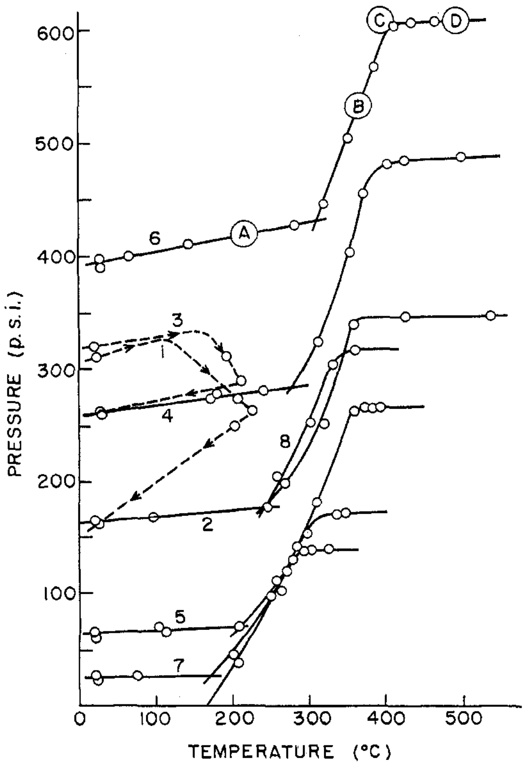

Figure 8.—Experimental data for the ytterbium–hydrogen system at high pressure.

The X-ray powder diffraction photographs of $CeH_{2.97}$ revealed that the fcc cell constant was 5.539 ± 0.001 A. The α_1–α_2 doublet was not resolved in the back-reflection region; nevertheless, accurate measurement of 15 well-defined diffraction lines to 70° was possible. Previous authors report considerable difficulty in their evaluation of *a* for cerium hydride specimens with compositions approaching CeH_3. These difficulties were due to the broadness of the diffraction lines because of the near amorphous state of the material prepared at low temperatures. These difficulties were not encountered in this determination since the hydride was well annealed during the high-pressure, high-temperature experiments.

Ytterbium–Hydrogen.—This system was also studied using the double-walled bomb. The low-pressure reaction of ytterbium metal with hydrogen yielded a sample with the composition $YbH_{1.90}$. The line was then pressured to approximately 20 atm and the $YbH_{1.90}$ heated for several hours (Figure 8, curve 1). Additional absorption occurred and the resulting hydride composition was calculated to be $YbH_{2.37}$, *i. e.*, the new, higher hydride.

A dissociation run (Figure 8, curve 2) to obtain *P–T* data was made on this sample at an initial pressure of 11 atm and no significant change in the final composition was observed. The hydrogen pressure over the hydride was again increased to roughly 22 atm (Figure 8, curve 3) which resulted in the absorption of additional hydrogen and preparation of $YbH_{2.57}$. This was observed to be the approximate limiting composition of the hydride during the many high-pressure dissociation experiments. The composition was determined analytically at the end of the initial experiments and found to be $YbH_{2.55\pm0.05}$.

Plots of pressure *vs.* the inside bomb (sample) temperature are shown in Figure 8. Curves labeled 1 and 3 are the above-mentioned absorption runs while the remainder are desorption runs. Curves 1–5 were carried out on the original sample, while curves 6–9 were carried out using the ytterbium hydride residues which were replaced in the bomb subsequent to earlier removal for examination. The over-all composition of the hydride residues caclulated from the weights of the samples of known composition was $YbH_{2.26}$. An initial absorption run was performed starting at 31 atm of hydrogen. The resulting composition of the solid phase was calculated to be $YbH_{2.53}$. The properties of the higher ytterbium hydride removed after run 5 are described the following paper.[13]

The curves in Figure 8 have three characteristic parts. Sections A and B have their previous meanings. Point C corresponds to the limiting minimum composition of the hydrogen-deficient orthorhombic ytterbium dihydride, and section D again corresponds to section A, an isochore of hydrogen. The composition of the hydride at the point on the curves marked C was consistently found to be $YbH_{1.9}$ and was in agreement with previous results observed in this laboratory.

Figure 9 shows isotherms obtained from the curves in Figure 8. Although there are only a few experimental points to describe the plateaus, the isotherms are reasonably well defined and present a rather asymmetric shape, tailing upward toward H:Yb = 2.6. The left limit lies along the dashed line drawn through the 600° isotherm from the low-pressure data up through the limiting composition found in this work. The plateaus in Figure 9 evidently correspond to the existence of two solid phases, one the cubic dihydride (discussed later[13]) and the other the cubic higher hydride. There is a certain resemblance to the gadolinium–hydrogen system in the hydrogen-rich area.[17]

A plot of the logarithm of the plateau pressures *vs.* reciprocal absolute temperature is shown in Figure 10. It is seen that the points are reasonably linear which can be described by the equation $\log P_{\text{atm}} = -1440/T + 3.54$, considering the reaction to be approximately

$$YbH_x \longrightarrow YbH_{1.9} + \frac{x - 1.9}{2} H_2$$

Following the arguments given in the preceding sections one can evaluate the van't Hoff isochore as

$$\log P_{\text{atm}} = \frac{\Delta H_{\text{diss}}}{2.303RT\frac{(x - 1.9)}{2}} + \text{constant}$$

Assuming that $x = 2.5$, a value of 6.6 ± 0.3 kcal/mole of H_2 is calculated for the heat of dissociation. Although Sturdy and Mulford[17] do not give a value for the heat of dissociation of $GdH_{\sim 3}$, it is possible to extract the data from their Figure 5, with which one can construct a van't Hoff plot of the plateau pressures. The equation obtained is

$$\log P_{\text{mm}} = -2620/T + 6.79$$

and a similar evaluation of ΔH_{diss} assuming that the reaction is

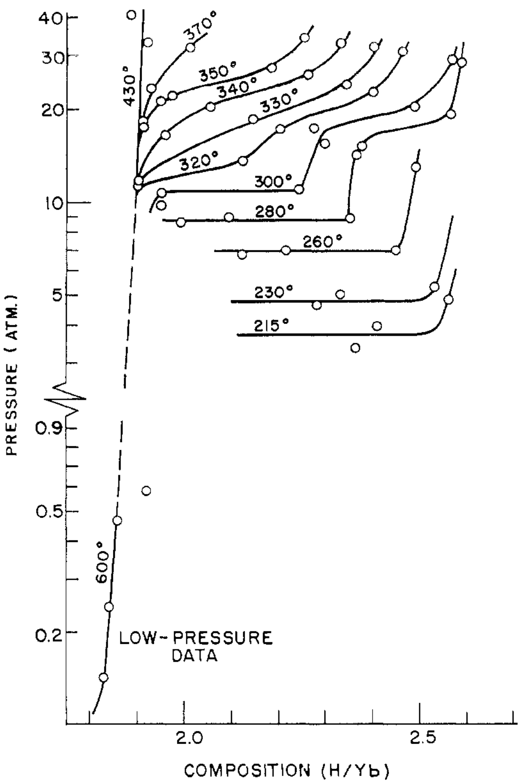

Figure 9.—Isotherms for the ytterbium–hydrogen system.

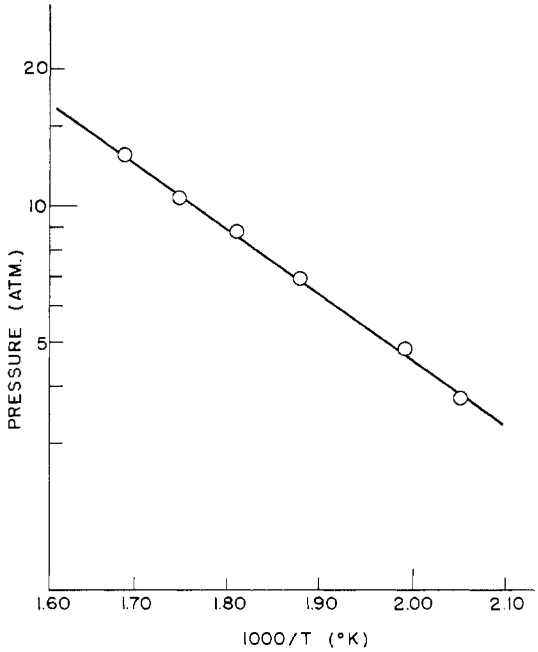

Figure 10.—Log *P vs.* reciprocal temperature plot for the region YbH_2–$YbH_{2.6}$.

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[17] G. E. Sturdy and R. N. R. Mulford, *J. Am. Chem. Soc.*, **78**, 1083 (1956).

$$GdH_{2.9} \longrightarrow GdH_{2.3} + 0.3H_2$$

gives approximately 12.0 kcal/mole of H_2.

Attempted Preparation of a Higher Hydride of Europium.—Two separate experiments were carried out using approximately 30-mg pieces of pure europium metal. The metal was placed in a small length of silica tubing, the bottom end of which had been drawn out and sealed. The silica tube was suspended by a platinum wire hung from the electrodes of the spark plug thermocouple connector. The length of the wire was such that the europium metal was positioned near the bottom of the inner bomb when the double-walled sample bomb was in place. After securing the bomb, etc., it was pressured to approximately 41 atm with hydrogen from the uranium hydride reservoir. The specimen was heated to roughly 500° and maintained at that temperature for several hours. The conditions of the two separate experiments were maximum pressures of 33 atm at 400° and 41 atm at 500°, respectively. After each experiment the hydrides were allowed to cool slowly. In each case, the silica tube containing the europium hydride was removed from the bomb into a protective atmosphere, and a portion of the hydride was forced into the capillary end of the tube, which was sealed off. This specimen was examined by X-ray powder diffraction techniques and the europium hydride remaining in the upper section of the tube was analyzed for hydrogen.

Analyses of these samples showed that the composition of each was $EuH_{1.8\pm0.06}$. The X-ray examination showed only the orthorhombic europium dihydride phase to be present along with a small amount of Eu_2O_3.

A third attempt was made to prepare a higher europium hydride using a much larger specimen of europium metal (2.83 g of extruded rod in the steel bomb; no silica was used). In this way, it was possible to determine from the *P–V–T* relationships whether a higher hydride formed under pressure, possibly decomposing when the pressure was dropped to atmospheric. After outgassing under vacuum, the europium was pressured with hydrogen at 41 atm at room temperature for 96 hr and then maintained at 303° for 48 hr at 61.2 atm. Finally, it was cooled to room temperature during the course of a 7-day period, the pressure being maintained. The *P–V–T* data revealed that at no time did the H:Eu ratio ever exceed 1.95 ± 0.03, and, after cooling, analysis (by dissolving in HCl and measuring the volume of H_2) confirmed that the material was dihydride.

Attempted Preparation of Scandium Trihydride.—The double-walled bomb was loaded with 1.02 g of pure scandium metal, attached to the high-pressure line, and evacuated, and then hydrogen was admitted from the UH_3 reservoir to 35 atm. The metal was heated to approximately 350° and kept at this temperature for several hours, after which it was cooled very slowly. The final pressure was 13.2 atm. The composition of the hydride was calculated to be $ScH_{2.02\pm0.03}$.

The X-ray powder diffraction photograph showed the presence of an fcc major phase along with several other lines which could not be ascribed either to the oxide or to the metal. These lines were too few in number and too weak to be indexed. Determination of the lattice constant of the fcc phase after correcting for film shrinkage and absorption gave a = 4.7835 A; thus, this phase corresponds to the dihydride observed by McGuire and Kempter.[18]

It is possible but unlikely that the extra lines do belong to a higher hydride phase of scandium. Possibly higher pressures and/or lower temperatures are required or perhaps some mechanical crushing of the sample while in hydrogen could effect preparation of a higher hydride.

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[18] J. C. McGuire and C. P. Kempter, *J. Chem. Phys.*, **33**, 1584 (1960).