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THE HYDRIDES OF THE RARE-EARTH METALS

V. I. Mikheeva and M. E. Kost

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INTRODUCTION

Whilst developing methods of physicochemical analysis, Kurnakov has paid particular attention to one of the fundamental questions of inorganic chemistry — the definition of the concept of a chemical compound and its relation to the concept of a solution[1,2].

The concept of "berthollide" phases, with no singular points, was put forward by Kurnakov in his study of metallic alloys and has since proved applicable to other classes of inorganic compound. In particular, Kurnakov has pointed out[1] that hydrides of the transition metals form interesting examples of phases of variable composition. Kurnakov considered that berthollide phases are based on compounds present in a dissociated state. Deeper study of the properties of metallic berthollide compounds[3,4] led to the theory that the metals were exhibiting variable valency, the dissociation being regarded as a mobile equilibrium between different valency states of one of the components. In the study of metallic phases, however, such a conclusion can only be reached from a study of the composition–property diagrams constructed both experimentally and on the basis of the law of mass action. It is impossible to prove the existence of different compounds within a range of metallic berthollide phases either by preparative methods or by X-ray structural analysis.

Work in recent years has shown that the chemistry of the hydrides reveals greater possibilities for understanding the nature of phases of variable composition than the chemistry of metals, since in the study of the former the construction of the composition–property diagrams can be supplemented by synthesis of the hydrides and their derivatives by reaction between the metal salts and various reducing agents in non-aqueous media. The unique position of hydrogen relative to the other elements leads to great variety in its compounds. The fact that hydrogen reacts with almost all the elements in the Periodic Table to form many types of chemical bond makes it possible to clarify the chemical character of other elements from the properties of their compounds with hydrogen.

In recent years considerable attention has been paid to the hydrides of the rare-earth metals, because of their chemical nature and the possibility of their practical application in metallurgy, vacuum technology, inorganic synthesis, etc.

In spite of the fact that rare-earth metal hydrides have been known for a considerable time, they had not until recently been studied in sufficient detail to enable any conclusions to be drawn regarding the nature of the chemical bonding of the hydrogen in these compounds.

An increasing amount of work devoted to their preparation, composition, and properties has appeared in the past few years. The aim of the present article is to summarise the published material in this field.

I. Reaction of the Rare-Earth Metals with Hydrogen

A general method for the preparation of the rare-earth metal hydrides is by the direct reaction between the metal and hydrogen. Sometimes the reaction proceeds fairly vigorously even at room temperature, but in other cases direct hydrogenation by molecular hydrogen at low temperatures is fairly slow. When this is so, for example with cerium, the metal is given a preliminary thermal treatment by heating in vacuo[5]. Several workers have related the resultant activation to the formation of microscopic cracks which facilitate the penetration of hydrogen into the metal[6]. It has also been suggested that the activation is related to the dissolution, at the high temperature, of cerium oxides blocking the metal surface. Dialer[7,8] has shown that the

activation of cerium by thermal treatment is related to the conversion of the β-form of the metal, which is inert towards hydrogen, to the active γ-form.

In recent years, hydrides of the transition metals have also been prepared by exchange reactions in aqueous and non-aqueous media, such as the well-known method for the preparation of copper hydride by the reaction between copper salts and hypophosphites in aqueous solution [9,10]. This method, however, is not generally applicable to the rare-earth elements, in view of the marked chemical reactivity of their hydrides.

The hydrides of the elements of the iron family and the vanadium and tungsten sub-groups can be obtained by the reaction between their halides and phenyl magnesium bromide in an atmosphere of hydrogen [11-16]. The hydrides of zinc and cadmium are obtained by the reaction with lithium aluminium hydride in ethereal solution [17]. Analogous methods have been tried for the rare-earth metals. The reaction between ethereal solutions of cerium bromide and lithium aluminium hydride gives not the simple hydride but a yellow precipitate of the double hydride of cerium and aluminium $Ce(AlH_4)_3$. [18-20]

The synthesis of double boro- and aluminohydrides of many of the transition metals [21-22] is important in confirming the existence of their simple hydrides. The generally-accepted principle that simple compounds can be stabilised by complex formation, suggests, for example, that the existence of the compound $M(BH_4)_n$ provides evidence that the existence and synthesis of the simple compound MH should be possible.

1) Lanthanum and Hydrogen

According to Winkler [23], Matignon [24], Muthmann et al. [25-27], Sieverts [28], and others, "lanthanum mischmetall", i.e. an alloy of lanthanum with smaller quantities of other rare-earth metals, reacts with hydrogen when finely divided even at room temperature. As the hydrogen is absorbed, voluminous grey-black platelets separate from the metal particles, since the hydrogenation of the lanthanum is accompanied by a 13% increase in volume.

The composition of lanthanum hydride, according to Winkler [23], corresponds to the formula LaH_2 (1.43 wt. % H, 66.7 at. % H), and according to Muthmann and Kraft [27], to the formula LaH_3 (1.95 wt. % H, 69 at. % H). Recent data [29] indicate that saturation of lanthanum with hydrogen at room temperature gives a product of composition LaH_3. The preparation of the deuteride LaD_3, with properties similar to those of lanthanum hydride, has been reported by Viallard [29].

According to Sieverts [30], the density of the lanthanum hydride $LaH_{2.76}$ is 5.83 g/cm^3, while that of LaH_2, calculated from X-ray diffraction data, has been found to be 5.14 g/cm^3. [31]

The heat of formation of a hydride with composition $LaH_{2.76}$ is 40.09 kcal/mole H_2 [28], i.e. it is of approximately the same order of magnitude, per unit valency, as the heat of formation of the alkali and alkaline-earth metal hydrides. According to Mulford and Holley [32], the heat of formation of lanthanum dihydride is slightly higher, and equal to 49.7 kcal/mole H_2.

Sieverts [5,30,33] found that the hydrogen content of lanthanum hydride specimens depends on the pressure of hydrogen above the metal, and that for the same hydrogen content, the pressure increases with increase in temperature. He therefore regards lanthanum hydride not as a definite compound, but as a solid solution of hydrogen in lanthanum. More accurate measurement of the dissociation pressure of lanthanum hydride has shown, however, that the pressure is constant up to the composition LaH_2 [32]. When the lanthanum absorbs greater quantities of hydrogen, there is a sharp increase in the dissociation pressure. The authors [32] conclude that two solid phases exist in the range $La-LaH_2$, while the range LaH_2-LaH_3 consists of a single phase, probably a solid solution of hydrogen in lanthanum dihydride.

In recent years lanthanum hydride has been studied a great deal, particularly by X-ray diffraction methods. Rossi [34,35] found that a specimen containing 200 cm^3 H_2 per g of metal ($LaH_{2.5}$) has a cubic lattice with a = 5.63-5.64 Å. Work by Holley, Zachariasen and others (involving X-ray and neutron diffraction studies [31]) on the dependence of the equilibrium pressure on the temperature and concentration [32] showed, together with microstructural examination, that below a hydrogen content corresponding to the composition LaH_2 (1.43 wt. % H, 160 cm^3 H_2 per g), the alloys consist of two phases — the metal and the hydride. The hydride LaH_2 has a face-centred cubic lattice of the CaF_2 type with a = 5.667 Å, and is able to dissolve more hydrogen: at the approximate composition $LaH_{2.39}$ (70.6 at. % H) the lattice parameter decreases to 5.63 Å. The extra hydrogen atoms in the hydrides containing more hydrogen than corresponds to the formula LaH_2 are randomly distributed in the octahedral holes of the face-centred cubic lattice. It has been suggested that a hydrogen pressure of more than one atmosphere is necessary to obtain a product with the composition LaH_3.

Earlier work by Stalinsky [36] on specimens of composition LaH_2-LaH_3 showed a change in the parameter of the face-centred cubic lattice within the range 5.66 Å to 5.60 Å. Measurement of the density of specimens of composition $LaH_{0.1}-LaH_{2.97}$ by the same author confirmed the contraction of the crystal lattice in the range between LaH_2 and LaH_3. Analogous data on the existence of two phases in the range $LaH-LaH_2$ were obtained by Dreifus-Allain [37-38], who showed that in the gradual hydrogenation metal and hydride exist together up to hydrogen pressures of 2.9 mm Hg. Above this pressure the lattice changes sharply and only the hydride remains. Similar effects were observed in the combination of lanthanum and deuterium [39].

The La-H phase diagram has recently been studied using a high-temperature powder camera [40]. It was found that even when the hydrogen content is extremely low, the hexagonal modification of lanthanum changes above 240° to the high-temperature modification with a = 5.29 Å and is not re-formed, even when cooled in liquid nitrogen.

In 1957 Stalinsky studied the magnetic properties of lanthanum hydrides [41], and found that the magnetic susceptibility decreases with increase in the hydrogen content. In the range $La-LaH_2$, the susceptibility decreases with increase in temperature in the range 120°-290°K, whereas that of specimens of composition LaH_2-LaH_3 remains constant.

Measurement of the electrical conductivity in the homogeneous region of the La-H system (LaH_2-LaH_3) has shown that the hydride is a semiconductor [42].

2) Cerium and Hydrogen

Cerium is the most readily available lanthanide, and its hydride has been studied in most detail. The chemical and physical properties of the rare-earth metal hydrides are typified by those of the cerium compound.

As early as 1891 Winkler [23] showed that the cerium which is obtained as a spontaneously inflammable dark brown powder by the reduction of cerium oxide with magnesium

contains a considerable quantity of hydrogen; he even suggested that a definite compound CeH_2 (1.41 wt. % H) was formed. He also suggested that the reaction of cerium with hydrogen requires the high temperature reached in the reaction with magnesium and also that the cerium must be present in the freshly-reduced state. Matignon[24], however, obtained cerium hydride by direct hydrogenation of the compact metal.

The hydrogenation of cerium was subsequently studied by Muthmann and Kraft[27], Muthmann and Bauer[25], Kellenberger and Kraft[43], Whitehouse[44], Lipsky[45], Dafert and Miklaus[46], and Zhukov[47]. In the nineteen-twenties the hydrides of the transition metals and the hydrogenation of cerium in particular were investigated by Sieverts et al.[5,28,33,48], but the absence of data on the hydrides of cerium and the other rare-earth metals in the literature of the thirties and forties shows that interest in these compounds had then weakened. In the fifties, however, the study of the rare-earth hydrides, and of cerium hydrides in particular, developed simultaneously in a number of countries, and new and interesting results appeared.

The kinetics of cerium hydrogenation. According to Muthmann and Kraft[27], metallic cerium absorbs hydrogen at 250°–270° to form a reddish-brown mass containing 1.74–3.19 wt. % H (average 2.4 wt. % H). Zhukov[47] established that cerium starts to react with hydrogen at 300° and that the reaction is extremely rapid at 400°; in 1923 Sieverts[5] concluded that cerium was activated by heating or fusion for a short time in vacuo, after which the metal starts to absorb hydrogen even at room temperature.

In 1948 Dialer[49] studied the relationship between the rate of absorption of hydrogen by pure cerium at 20° and the temperature of the preliminary heat treatment of the metal. He found that increase in the temperature of the pre-treatment increases the rate of absorption of hydrogen up to an optimum value corresponding to the thermal treatment at 650°. The decrease in the activity of specimens after pre-treatment at 845° was explained by the author as due to fusion of the cerium, leading to a decrease in the number of active hydrogenation centres. In subsequent work Dialer and Rothe[7] established that β- and γ-cerium at room temperature[50,51] behave differently towards hydrogen: γ-Ce absorbs hydrogen without preliminary thermal treatment, while β-Ce does not react with hydrogen. γ-Ce can be converted to β-Ce by heating to 70°.

Mikheeva and Kost[20,52] studied the rate of reaction of cerium with hydrogen at different temperatures and showed that compact metallic cerium will absorb hydrogen even at room temperature without preliminary thermal treatment, if the hydrogen is thoroughly purified. The curve showing the relationship between the hydrogenation time (to saturation) and the temperature (Fig. 1) shows three branches — — two descending and one ascending.

Comparison of these data with the composition curve (Fig. 2, curve *a*) shows that the descending branches of the curve in Fig. 1 correspond to the formation of cerium trihydride and dihydride, while the decrease in the rate of hydrogenation with increase in temperature corresponds to the formation of hydrides of variable composition in the range CeH_2–CeH_3.

The composition of cerium hydrides. Sieverts and Roell[33] showed that the quantity of hydrogen absorbed by cerium decreases with increase in the temperature, and that the smooth temperature–composition curve for the hydride shows a sharp inflection at 1100°–1200°,

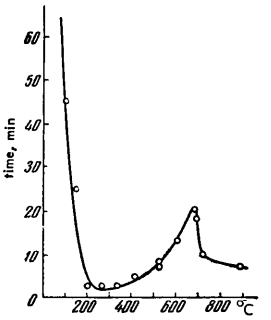


Fig. 1. Relationship between the time of hydrogenation of cerium and temperature[20].

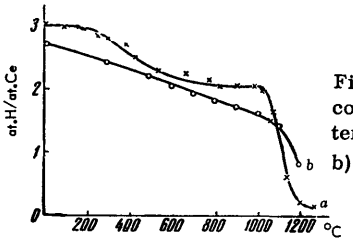


Fig. 2. Relationship between the composition of cerium hydrides and temperature: a) Mikheeva and Kost[20]; b) Sieverts and Roell[33].

indicating that cerium hydride decomposes appreciably above 1100° (Fig. 2, curve *b*).

Since practically no reaction between cerium and hydrogen is observed below 0°,[25] most authors achieve maximum saturation of the hydrides by rapid cooling to room temperature.

Muthmann[27] obtained a high degree of saturation of cerium by hydrogen, but the reproducibility of the separate experiments was poor (Table 1). Sieverts[5,28], using the thermal treatment, obtained more stable results, but the hydrogen concentration of his specimens was much lower, and did not reach the composition CeH_3. A recent paper on the rare-earth metal hydrides[31] still reports that it is impossible to obtain cerium "trihydride" without using increased pressure of hydrogen.

Using improved methods for purifying the starting materials Dialer[49] in 1948 prepared cerium hydride of stoichiometric composition CeH_3 from mischmetall, the hydrogen content being referred to pure cerium; in 1955 he obtained cerium trihydride by hydrogenating pure cerium at room temperature[7,8]. This was also achieved by Mikheeva and Kost[20,52] showed that the curve relating the composition of cerium hydrides and temperature (Fig. 2, curve *a*) has two plateaux corresponding to the compounds CeH_3 and CeH_2 (contrary to Sieverts' data[33]). This shows that the two hydrides exist over definite temperature ranges[20]. The trihydride is obtained by the reaction between cerium and hydrogen at room temperature, and the dihydride can be obtained by heating the trihydride for half an hour at 400°. The composition of the cerium hydride formed at room temperature is independent of the hydrogen pressure, and the limiting hydrogen content corresponds to the formula $CeH_{3.15}$[20].

The dissociation pressure of cerium hydrides. In their first experiments, Muthmann and

Bauer[25] found that the dissociation pressure of cerium hydride for a given temperature was not reproducible, being different after reheating. The authors concluded that the dissociation of cerium hydride was irreversible in the temperature range up to 740°. They ascribed this phenomenon to an irreversible change in the molecular structure of the hydride.

In a study of the dissociation isotherms at 480° and 450°, Zhukov[47] found that the pressure remained constant (~ 1 mm Hg) up to 160 cm^3 H_2 per g Ce, i.e. up to a composition corresponding to cerium dihydride. Further increase in the hydrogen content leads to a sharp increase in the pressure. Zhukov took this to indicate the existence of the compound CeH_2.

Sieverts and Müller-Goldegg[5] studied the isotherms over a wider temperature range. Detailed study of the 800° isotherm showed that they all consist of three clearly-defined branches. The first ascending branch shows a very slight increase in the pressure from 0 to several mm Hg. This is followed by a horizontal branch almost coinciding with the x-axis, and this in turn is followed by a third branch which rises steeply. Analogous curves with good reproducibility were obtained by Dialer[49].

Owing to inaccuracy in the measurements at low pressures, the start of the third branch was displaced with decrease in the temperature, which contradicted Zhukov's conclusion that cerium dihydride is formed. More detailed study with accurate measurement of the low pressures[32], however, subsequently confirmed Zhukov's conclusion that cerium dihydride exists up to 800° (Fig. 3).

Fig. 3 shows that the dissociation pressure at 500°–800° remains constant up to the approximate composition CeH_2, which indicates that two phases exist in this range: the metal, saturated with hydrogen, and cerium dihydride. When one of the phases disappears (in this case the metal) a very slight increase in the hydrogen content leads to a sharp increase in the pressure.

The isotherms for lower temperatures (Fig. 4) show that the CeH_3–CeH_2 system most probably consists of a solid solution of hydrogen in cerium dihydride[32].

The structure of cerium hydrides. Conclusions based on the dissociation pressure of cerium hydrides are confirmed by recent X-ray diffraction studies.

Until recently the only such work was by Rossi[35], who reported that cerium hydride has a face-centred cubic lattice with lattice parameter a = 5.61 Å. Removal of hydrogen by evacuation at 530° leads to the appearance of a second phase with a slightly smaller lattice period.

In 1955, Zachariasen et al.[31] described the crystal structure of rare-earth metal hydrides, including cerium hydrides of composition CeH–$CeH_{2.7}$, and found that specimens containing less than two hydrogen atoms per metal atom consist of a mixture of metal and hydride with lattice parameter a = 5.581 ± 0.001 Å. Close to the composition CeH_2, the lattice of the metal disappears leaving only that of the hydride CeH_2, which is of the CaF_2 type with the above parameter. Further increase in the hydrogen content causes a gradual decrease in the lattice parameter, which reaches the value a = 5.540 ± 0.003 Å for $CeH_{2.47}$. Specimens of higher hydrogen content were not studied.

Kost and Gol'der[53] obtained analogous data showing the presence of two phases in the range $CeH_{0.2}$–CeH_2, with lattice parameters a' = 5.13 Å and a'' = 5.55 Å. They also studied specimens of higher hydrogen content and confirmed

TABLE 1. Composition of cerium hydride showing maximum saturation with hydrogen.

At. H / At. Ce	Deviation in separate experiments	Method of analysis	References
3.4	±0.9	from increase in weight	27
3.03	±0.2	»	46
2.75	±0.05	»	5
2.60	±0.1	»	28
3.00	±0.01	by ignition and volume measurement	49
3.00	±0.1	by volume measurement	20,52

that the lattice parameter decreases when cerium dihydride absorbs more hydrogen. Specimens of composition $CeH_{2.73}$ consist of a homogeneous phase with parameter a = 5.53 Å. As the composition approaches CeH_3, the lines in the powder diffraction pattern become broader, which makes exact calculation of the lattice parameter difficult.

Auphassorho[54–56] detected two new phases. As cerium dihydride absorbs hydrogen and approaches the composition CeH_2, a new phase (γ) with parameter 5.645 ± 0.003 Å was observed in addition to the β-phase with parameter 5.581 Å. With further absorption of hydrogen, the intensity of the lines of the β-phase decreases, with a simultaneous decrease in the parameter of the γ-phase. When the lines corresponding to the β-phase have disappeared completely, at a hydrogen pressure of 4 mm Hg, a single lattice with parameter 5.634 ± 0.0004 Å remains. Increase in the hydrogen pressure to 38 mm Hg leads to a decrease in the parameter to 5.612 ± 0.003 Å. The author relates the appearance of this new phase to a difference in the hydrogen distribution

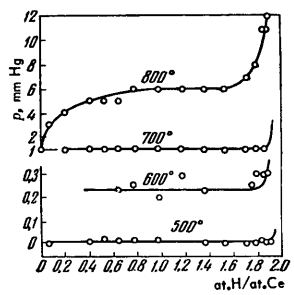


Fig. 3. Dissociation-pressure isotherms for cerium hydrides in the range Ce – CeH_2.[32]

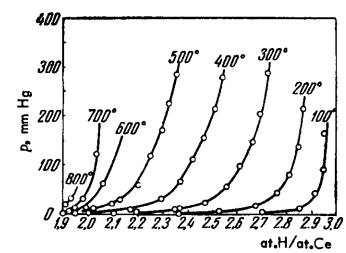


Fig. 4. Dissociation-pressure isotherms for cerium hydrides in the range CeH_2–CeH_3.[32]

in the cerium lattice, assuming that in the β-phase all the tetrahedral holes in the cubic face-centred lattice are occupied, while in the γ-phase the hydrogen atoms are situated in octahedral holes. In his most recent work[56], the formation of another phase in the Ce–H system is reported. Specimens containing this phase were obtained by prolonged heating (500 h at 300°) of cerium dihydride with lattice parameter a = 5.590 Å, which yielded a hydride of composition $CeH_{0.7\pm0.2}$ with lattice parameter a = 5.04 ± 0.01 Å. The author attributed the appearance of this phase to redistribution of the hydrogen atoms in the octahedral holes. In view of the lattice contraction which takes place, he suggested that the new hydride is analogous in chemical character to the alkali-metal hydrides.

The physical properties of cerium hydrides. The earliest pyknometric data obtained by Sieverts and Gotta[28] using petroleum ether as flotation medium gave the average density of material of composition $CeH_{2.69}$ as 5.55 (±3%) at 25°, compared with the value 6.734 for the original cerium. The absorption of hydrogen thus leads to a decrease in the density by 17.5%, i.e. an increase in specific volume of 21.6%.

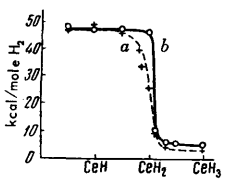


Fig. 5. Heat of formation of cerium hydrides vs. composition[8]:
a) calculated; b) experimental.

Kost and Gol'der[53] measured the density of hydride specimens in the concentration range $CeH_{0.2}$–CeH_3 by the "argon" method. The density–composition curve shows a decrease in the density with increase in the hydrogen content, followed by a minimum approximately at the composition CeH_2 (d_{20} = = 5.4 g/cm³) and a slight increase in the density with further approach to the trihydride composition (d_{20} = 5.5 g/cm³).

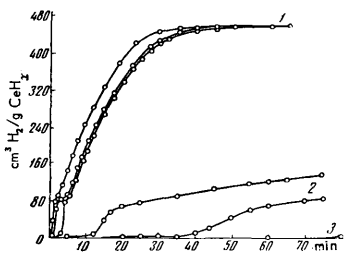


Fig. 6. Hydrolysis of cerium hydride[60]; 1) CeH_3 at 20°; 2) CeH_3 at 0°; 3) CeH_2 at 20°.

The heat of formation of cerium hydride, determined by dissolution in hydrochloric acid[28], amounts to 42.26 kcal per mole of combined hydrogen. A more detailed study of the heat of formation of cerium hydrides of different composition was made by Dialer[7,49] who constructed log p vs. $1/T$ curves from data on the dissociation pressure of the hydrides. The curve for the heat of formation of various hydrides (Fig. 5, curve a) shows good agreement with the data from the direct calorimetric determination involving dissolution of the cerium hydrides in acid (Fig. 5, curve b). Both curves show a sharp drop close to the composition CeH_2, which indicates that the attachment of the third hydrogen atom to the cerium dihydride is accompanied by a much smaller heat of reaction than the addition of the first two hydrogen atoms.

The change in the electrical conductivity of cerium powders during hydrogenation is of particular interest. Daou[57] was the first to overcome the considerable experimental difficulties involved and measure these changes. He found that the resistance increases by a factor of several hundreds during the hydrogenation of cerium up to a cerium : hydrogen ratio of 1 : 1, after which the resistance starts to decrease. The hydrogenation was found to be reversible. In 1958 Daou improved his technique and measured the electrical resistance of cerium during hydrogenation up to a composition $CeH_{2.4}$ [58]. Under these conditions the resistance of the cerium decreases linearly by 30% as the composition CeH_2 is approached ($CeH_{1.8}$), after which it rises steeply. The author attributed this to the increased metallic character of the hydride CeH_2 resulting from movement of the 4f electrons to the s level and back, i.e. he put forward an explanation similar to that of Zachariasen et al.[31]. In the same work the author detected an anomalous change in the resistance during thermal treatment in the composition range close to CeH.

The magnetic properties of the Ce–H system were studied by Albany[59], who detected anomalous ferromagnetism in the range $CeH_{1.9}$–CeH_2. The author himself suggested, however, that this effect was due to iron impurities.

The chemical properties of cerium hydrides. Cerium hydride with highest hydrogen content is a highly reactive brittle flaky grey-blue material. The freshly-prepared hydride reacts with nitrogen even at room temperature[45] and when heated to 800°–900° is completely converted to the nitride. It is spontaneously inflammable in air[23,25] and burns to form a mixture of oxide and nitride. This makes it difficult to work with, but a short treatment with dry carbon dioxide brings about surface passivation, which makes it possible to handle specimens for short periods in air[60].

Cerium hydride dissolves readily in dilute acids with evolution of hydrogen:

$$CeH_3 + 3HCl = CeCl_3 + 3H_2.$$

This reaction is used for the quantitative estimation of the hydrogen in these hydrides.

Cerium trihydride reacts fairly vigorously with water even at 0°,[60] liberating hydrogen and forming white cerium hydroxide:

$$CeH_3 + 3H_2O = Ce(OH)_3 + 3H_2.$$

Cerium dihydride reacts with water much more slowly than the trihydride (Fig. 6)

Cerium hydride precipitates many heavy metals from solutions of their salts. It forms explosive mixtures with nitrates and perchlorates. No vigorous reaction is observed with gaseous chlorine at room temperature, but an explosion takes place on heating. The reaction with hydrogen bromide at 500°–600° is vigorous and can be used to prepare anhydrous cerium bromide[60].

Cerium di- and trihydride differ considerably in their thermal stability. The trihydride begins to decompose at ~200°, whereas the dihydride is stable up to 800°–900° [20] (Fig. 7). Vigorous decomposition begins only after fusion at 1080°, and even at 1200° the hydrogen is not removed completely [20].

Double hydrides of cerium and aluminium. Until recently nothing was known of double hydrides of the rare-earth metals [21, 22], but an aluminohydride of trivalent cerium has now been synthesised [18–21]. The double hydride $Ce(AlH_4)_3$ is obtained by the reaction between cerium bromide and an ethereal solution of lithium aluminium hydride at -79°. [20] It consists of an extremely reactive yellow powder, which decomposes gradually to the elements when heated to -40°.

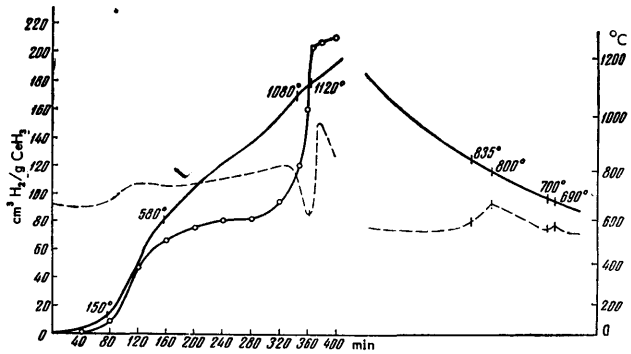


Fig. 7. Thermogram for the CeH_3 decomposition [20].

3) Praseodymium and Hydrogen

According to Muthmann and Beck [61], praseodymium does not react with hydrogen at room temperature and absorbs the gas actively only at 300°–400° with the formation of a brittle green product.

According to Sieverts and Roell [60], hydrogenation yields a product with composition close to PrH_2, but the authors suggest that the substance is not a definite compound but a solid solution, since the compounds PrH_2 and PrH_3 contain 1.40% and 2.08% of hydrogen respectively, while the material obtained on hydrogenation contains 1.68% H. The hydrogen pressure–hydrogen content curves are analogous to those for the cerium–hydrogen system [28, 32].

The density of the material of composition $PrH_{2.84}$ is 5.56 g/cm³, i.e. 14.6% less than that of the compact metal; the heat of formation of the same specimens is 39.52 kcal per mole H_2 [41]. In a recent paper [32], the heat of formation of PrH_2 was calculated from data for the dissociation pressure of the hydride and found to be 47.8 kcal/mole.

Rossi [35] has investigated the structure of praseodymium hydride and found that the β-modification has a hexagonal close-packed lattice with a = 3.65 Å and c/a = 1.61. In 1955 Mulford and Holley studied the dissociation pressure and crystal structure of praseodymium hydride and concluded that two phases, with cubic face-centred lattice, exist in the range $Pr–PrH_2$, after which a solid solution of hydrogen in the dihydride is formed (a = 5.517). The density of the dihydride is 5.65 g/cm³. [31]

4) Neodymium and Hydrogen

The properties of neodymium hydride are analogous to those of praseodymium hydride [24,31,32,61,62]. On hydrogenation metallic neodymium is converted to a dark-coloured powder with a hydrogen content corresponding approximately to the formula NdH_2. The dissociation-pressure isotherms and X-ray diffraction data [31,32] indicate the existence of neodymium dihydride with lattice parameter a = 5.470 Å and density 5.94 g/cm³. The heat of formation calculated from the dissociation-pressure data is 44.8 kcal [32].

5) Samarium and Hydrogen

Metallic samarium reacts with hydrogen at high temperatures forming a product of composition SmH_2, which dissociates readily on further heating [24]. Like the hydrides of other rare-earth metals, samarium hydride has a face-centred cubic lattice of the CaF_2 type with $a = 5.376 \pm 3$ Å and density 6.52 g/cm³. [23]

According to recent work [63], maximum saturation with hydrogen corresponds to the hydride SmH_3. There are reports [64] that samarium trihydride is isostructural with plutonium trihydride PuH_3, i.e. it has a hexagonal lattice [65,66].

6) Europium and Hydrogen

Europium hydride and deuteride have been studied by Korst and Warf [63,67]. In contrast to the behaviour of other rare-earth elements, the absorption of hydrogen by europium up to the composition $EuH_{1.96}$ is accompanied by a considerable lattice contraction and a resultant increase in the density by 12.5% compared with the original metal.

The resemblance of europium hydride and deuteride to the salt-like hydrides is confirmed by their structure, which is analogous to that of strontium hydride SrH_2. Europium deuteride has lattice parameters a = 6.21 Å, b = 3.77 Å, and c = 7.16 Å (±0.02 Å) [67].

7) Gadolinium and Hydrogen

The conditions for the reaction of hydrogen and deuterium with gadolinium were first studied by Viallard [68,69] who found that hydrogen and deuterium react with gadolinium above 150° to form Gd_2H_3 or Gd_2D_3 respectively, and that Gd_2H_3 can be converted to GdH_2 by cooling in a current of hydrogen.

The compounds GdH_2 and GdD_2 are stable at room temperature, but dissociate when heated above 250°, forming the original compounds Gd_2H_3 and Gd_2D_3 [69]. The actual composition of these compounds, however, deviates slightly from these formulae.

The dissociation-pressure isotherms for gadolinium hydride have been constructed by Sturdy and Mulford [70]. In contrast to the systems formed by hydrogen with lanthanum, cerium, neodymium, and praseodymium, the gadolinium–hydrogen system gives isotherms with two horizontal plateaux: one in the range $Gd–GdH_2$ and one in the range $GdH_2–GdH_3$. This led the authors to suggest the existence of two hydrides GdH_2 and GdH_3, which has been confirmed by X-ray analysis [31]. The first plateau corresponds to the coexistence of metal and dihydride, with face-centred cubic lattice (a = 5.303 ± 0.001 Å), as in the cerium–hydrogen system.

The second horizontal plateau corresponds to the two-phase region GdH_2-GdH_3. Gadolinium trihydride is isomorphous with PuH_3 and has a hexagonal lattice with parameters $a = 3.73 \pm 0.01$ Å and $c = 6.71 \pm 0.02$ Å. The density of gadolinium dihydride calculated from the X-ray structure date is 7.08 g/cm³, while that of the trihydride is 6.57 g/cm³. [70]

The authors [64,70] have also given the phase diagram for the Gd–H system and have calculated the heat of formation of gadolinium dihydride, 46.9 kcal/mole.

8) Ytterbium and Hydrogen

According to Korst and Warf [63,67], the saturation of ytterbium with hydrogen to the composition YbH_2 leads to an increase in the density by 13.5%, as in the case of europium. The structure of ytterbium deuteride is analogous to that of SrH_2 and is orthorhombic with parameters $a = 5.871$ Å, $b = 3.561$ Å, and $c = 6.763$ Å. [60]

II. SOME PECULIAR FEATURES OF THE RARE-EARTH HYDRIDES

If we adopt the generally-accepted classification of inorganic hydrides [71–73] into the three classes — salt-like, covalent and metallic — we find that the hydrides of the rare-earth elements occupy a special position.

The salt-like hydrides are characterised by constant composition, electrovalent bonding, high heats of formation (30–40 kcal/mole H_2), and a density greater than that of the original metals (Proskurnin and Kazarnovskii [74]).

The volatile covalent hydrides formed by the elements in Groups IV–VII A also have constant composition and high heats of formation [75].

The class of metallic hydrides includes the hydrogen compounds of all metals in which the inner d and f levels are being filled. The products of the direct hydrogenation of these metals do not, in most cases, exhibit stoichiometric composition, and depend on the conditions under which the reactions are carried out. For most transition-metal hydrides, the composition is related to the hydrogen pressure by the equation [76,77]

$$m = k\sqrt{p_{H_2}}$$

or by the more exact formula derived by Fowler and Smithells [78]

$$\log m = 2.774 + 0.5 \log p - 0.25 \log T - \log d - \frac{\theta}{9.148\,T},$$

where m is the number of cm³ of hydrogen per 100 g of metal, p the pressure in mm Hg, T the absolute temperature, d the density of the hydride, and θ the heat of dissolution of hydrogen in the metal, in kcal/mole H_2.

The absorption of hydrogen by the transition metals is accompanied by a decrease in the density. Detailed study has shown, however, that within the transition metals there is a considerable difference in behaviour, and this is shown particularly clearly by the elements of the "extreme" groups. Thus, for example, the elements in Groups IB and IIB — copper, zinc and gold — are analogous to elements in the middle of the short periods (Be, B, Al) and under certain conditions form unstable volatile hydrides [78, 80], so that these may be put in a separate class of the so-called polymeric hydrides [81]. On the other hand, the elements in Groups III–V differ essentially from the typical metallic hydrides and resemble the salt-like hydrides in their heats

TABLE 2. Heat of formation of certain hydrides.*

Hydride	Heat of formation, kcal/mole H_2	References	Hydride	Heat of formation, kcal/mole H_2	References
LiH	42.68	82	PuH_2	32.5	84
NaH	27.2		$TiH_{1.75}$	36.0	85
KH	30.32		$ZrH_{1.92}$	40.5	86
CaH_2	46.6	73	$CrH_{0.26}$	3.8	28
BaH_2	40.96		$PdH_{0.59}$	8.59	87
SrH_2	42.2		Mo*	−14.0	88
$CeH_{2.69}$	42.26	28	Co	−14.55	
$PrH_{2.84}$	39.52		Cu	−18.3	
$LaH_{2.46}$	40.09		Ni	−5.9	89
UH_3	20.6	83	Fe	−5.9	

* The heats of formation of the hydrides of molybdenum and succeeding metals were found from the slope of the $\log S - 1/T$ isobars, using the equation $\log S = \log S_0 + 0.5 \log P - \frac{\theta_3}{9.148} T$, where S_0 and P are constants.

of formation (Table 2), the quantities of hydrogen which they absorb, and the shape of their solubility isobars [77]. Nekrasov therefore puts them in a separate class of "intermediate" hydrides [81]. The hydrides of the rare-earth elements, which are closest to the alkaline-earth elements, should undoubtedly show these "intermediate" properties even more clearly.

The density changes also show the similarity to the salt-like hydrides. It has been mentioned that in contrast to the case of the ionic hydrides, the formation of the rare-earth metal hydrides is accompanied by a considerable decrease in the density (Table 3). Recent work has shown, however, that the nature of the change in the density is not a fundamental criterion in the classification of the hydrides. Thus by comparing atomic and ionic radii, Dialer [90] has shown that, for cerium in particular, the decrease in the density on hydrogenation may result from the small change in the volume of the atom on ionisation. Dialer's calculations for cerium are compared with data for the alkali metals in Table 4. The last column shows the change in volume per unit valency on going from the atomic to the ionic state.

TABLE 3. Density changes on hydride formation [90]

Hydride	Density of metal, g/cm³	Density of hydride, g/cm³	Change in density, %	Change in specific volume, %
LiH	0.534	0.816	+52.3	−34.2
NaH	0.97	1.4	+44	−31.1
KH	0.86	1.47	+71	~−41
RbH	1.52	~2	~+33	−24
CsH	1.87	2.7	+44	−30
CaH_2	1.55	1.7	+10	−9
BaH_2	3.5	4.21	+20	−17
$CeH_{2.69}$	6.73	5.55	−17.5	+21.6
$PrH_{2.84}$	6.51	5.56	−14.6	+16.9
$LaH_{2.76}$	6.69	5.83	−12.8	+15.4
$TiH_{1.62}$	4.52	3.91	−13.5	+15.5
ZrH_2	6.79	5.47	−19.4	+24.5
$VH_{0.56}$	5.68	5.30	− 6.7	+ 7.2
$CrH_{0.26}$	~7.0	6.77	− 3.7	+ 3.7
$PdH_{0.55}$	11.87	10.76	− 9.4	+10.3

Analysis of the data in Table 4 shows that in the case of alkali and alkaline-earth metal hydrides, the volume change per unit valency ($\Delta v/n$) is much greater than the volume of the negatively charged hydrogen ion. These compounds are therefore formed with a decrease in volume, whereas the volume made available by the ionisation of cerium (to Ce^{3+})

TABLE 4. Change in the volume of metal atoms on ionisation [90].

Metal	Atomic radius, Å	Ionic radius, Å	Atomic volume, Å³	Ionic volume, Å³	$\frac{\Delta v}{n}$
Na	1.86	0.98	26.9	3.9	23.0
Rb	2.36	1.49	55.1	13.9	41.2
Ca	2.21	1.06	45.2	5.0	20.1
Ce	1.69	1.18	20.2	6.9	4.4
H^-		1.27	—	8.58	—

TABLE 5. The atomic volume of hydrogen in hydrides [91].

Hydride	Mol. volume of hydride, found experimentally	Mol. volume of hydride, calculated for $T = 0$	Zero-temperature volume of metal	Volume of H in the hydride *
LiH	9.8	9.6	12.6	(3.3)
NaH	17.4	17.1	22.8	5.7
KH	27.3	26.8	43.4	5.1
RbH	33.3	32.6	53.1	6.0
CsH	39.1	38.3	65.9	5.3
CaH_2	24.8	24.6	25.5	5.9
BaH_2	33.1	32.8	38	6.9
$LaH_{2,76}$	24.3	24.1	20.4	5.0
$CeH_{2,69}$	25.7	25.4	20.4	5.7
$PrH_{2,84}$	25.8	25.5	21.2	5.3
$VH_{0,56}$	9.73		9.9	1.3
$CrH_{0,26}$	7.72		7.4	1.2
$PbH_{0,55}$	9.97		9.0	1.8

* These values were obtained by the author by subtracting half the zero-temperature volume of the metal from the zero-temperature molar volume of the hydride, as required by the preceding calculations in the same work.

is insufficient to accommodate the hydrogen anions, so that the formation of an ionic bond in hydrides of the transition metals, and the lanthanides in particular, may be accompanied by a decrease in the density.

On the other hand, Table 5 gives Biltz's data for the volume of hydrogen in various hydrides, calculated from the measured density and the ionic volume of the metal in question (Table 5, column 4) in its other compounds [91].

The last column in Table 5 shows that the hydrogen in the rare-earth metal hydrides occupies the same volume as in the ionic hydrides, whereas the volume of hydrogen in the metallic hydrides is much smaller.

Analogous results were obtained by Libowitz and Gibb [92] in their calculation of the ionic radius of hydrogen in various hydrides (Table 6). They started from the normal oxidation state of the metal (Table 6, column 4) assuming that the fraction of the electrons not taken up by the hydrogen take part in the formation of a residual metallic bond, which is responsible for the electrical conductivity of these compounds. The radius of the electronegative hydrogen (Table 7) decreases regularly with increase in the electronegativity of the cation and hence it may be assumed that the radius of the hydrogen anion in the intermediate hydrides will be less than 1.37 Å.

Table 6 shows that the average value is in fact 1.29 ± 0.05 Å. Since in the case of a covalent or metallic bond the hydrogen atom has a radius of 0.27–0.80 Å, the authors conclude that the hydrogen in the intermediate hydrides is ionic in character.

On the other hand, until recently the chief indication of the difference between the rare-earth metal hydrides and the salt-like hydrides has been the absence of stoichiometric relationships in the former. Newer data indicate, however, that compounds exist in metal–hydrogen systems.

Accurate measurement of the dissociation pressures of the hydrides of lanthanum, cerium, praseodymium, neodymium, and gadolinium [32] has confirmed, and extended to other elements, the suggestion made by Zhukov in 1912 regarding the formation of cerium dihydride [47]. X-ray analysis also confirms the existence of these compounds and their coexistence with metal in the range $M-MH_2$ [31]. Some properties of these hydrides are given in Table 8.

Cerium dihydride is stable up to 900°–1000°, and starts to decompose rapidly only after fusion at 1060°–1080°. [20]

From the point of view of the relationship between a compound and a solid solution, the phases of variable composition in the range $MH_2 - MH_3$ are of particular interest. In the case of cerium, lanthanum, neodymium, and praseodymium, measurement of the dissociation pressure and X-ray analysis has shown the presence in this range of a continuous series of solid solutions whose density increases regularly with increase in the hydrogen content.

Comparison of this fact with data for the chemical reactivity of the cerium hydrides CeH_2 and CeH_3, of which the former exhibits more marked metallic character, while the latter is more reactive towards water, leads inevitably to the idea that there is a gradual change in the nature of the chemical bond within the limits of the solid phase CeH_2-CeH_3, i.e. to the suggestion that two valency forms of cerium exist together in equilibrium. The views of Daou and Auphassorho [56,58] are of interest in this connection.

The authors consider that the redistribution of hydrogen in the octahedral holes, which takes place in this range, leads to an increase in the ionic character of the bond, as in the salt-like hydrides. Auphassorho considers that this

TABLE 6. Radius of the hydride anion in the intermediate hydrides [92].

Hydride	M–H distance, Å	Cationic radius, Å	Oxidation state of cation	Correction for coordination number	H radius, Å
TiH_2	1.93	0.60	4+	0.08	1.25
ZrH_2	2.09	0.77	4+	0.08	1.24
LaH_2	2.45	1.04	3+	0.08	1.33
CeH_2	2.42	1.02	3+	0.08	1.32
PrH_2	2.39	1.00	3+	0.08	1.31
NdH_2	2.37	0.99	3+	0.08	1.30
SmH_2	2.33	0.97	3+	0.08	1.28
GdH_2	2.30	0.95	3+	0.08	1.27
AcH_2	2.46	1.11	3+	0.08	1.27
ThH_2	2.41	0.99	4+	0.08	1.34
PaH_2	2.32	0.90	5+	0.19	1.23
UH_2	2.32	0.86	6+	0.19	1.27
PuH_2	2.32	0.90	4+	0.08	1.34

TABLE 7. Radius of the hydride anion in the alkali metal hydrides [92].

Hydride	M–H distance, Å	Cationic radius, Å	Radius of H^- ion, Å
CsH	3.19	1.67	1.52
RbH	3.02	1.48	1.54
KH	2.85	1.33	1.52
NaH	2.44	0.98	1.46
LiH	2.05	0.68	1.37

TABLE 8. Properties of the dihydrides of certain rare-earth metals.

Element	Heat of formation of dihydride, kcal/mole	Lattice parameter, Å	Density, g/cm³	Relationship between dissociation pressure and temperature
La	49.7	5.667	5.14	$\log p = 10.758 - 10858/T$
Ce	33.9	5.581	5.43	$\log p = 7.708 - 7417/T$
Pr	47.8	5.517	5.65	$\log p = 10.229 - 10446/T$
Nd	44.8	5.470	5.94	$\log p = 9.370 - 9796/T$
Sm	—	5.376	6.52	—
Gd	46.9	5.303	7.08	—

is confirmed by the formation of a δ-phase in the cerium–hydrogen system, in which the hydrogen is distributed only in the octahedral holes, leading to a considerable contraction in the metal lattice, i.e. to a phenomenon characteristic of the formation of an ionic M–H bond.

Thus the solid phase CeH_2–CeH_3 in the Ce–H system is an extremely interesting example of a berthollide phase[2,3]. Within the range of homogeneity of this phase, we have a continuous transition from the compound CeH_2 with greater metallic-bond character (the hydrogen atoms arranged in the tetrahedral holes of the face-centred cerium lattice) to the compound CeH_3, with greater ionic-bond character (the hydrogen atoms arranged in both tetrahedral and octahedral holes in the lattice).

Further interesting data are provided by the gadolinium–hydrogen system[70]. Unlike the systems described above, this shows the formation of a new phase GdH_3, with hexagonal lattice, in the GdH_2–GdH_3 range. This difference is evidently explained by the fact that gadolinium trihydride, unlike the trihydrides of the other rare-earth metals, does not form solid solutions with the dihydride.

In spite of the fact that study of the dissociation pressure and X-ray analysis in the case of cerium, lanthanum, neodymium, and praseodymium give no direct indication of the existence of the trihydrides of these elements, there is indirect proof that such compounds exist. Thus the existence of the compound CeH_3 is suggested by the formation of the double hydride $Ce(AlH_4)_3$. At the same time, a fundamental difference between the trihydride CeH_3 and hydrides of composition intermediate between CeH_2 and CeH_3 is indicated by the definite and fairly wide range of temperature and pressure within which a hydride of definite stoichiometric composition is formed[8,20].

The data for the rare-earth elements cerium, lanthanum, neodymium, praseodymium, samarium, gadolinium, etc. may thus be taken as proving the existence of hydrides of composition MH_2 and MH_3.

While the rare-earth metals have many properties in common, such as the ability to combine directly with hydrogen with the evolution of heat, to form phases of variable composition, etc., certain individual features can also be distinguished — for example, the appearance of a trihydride of hexagonal structure in the case of samarium and gadolinium. It is also reported that gadolinium forms a compound Gd_2H_3. A more marked difference is shown by europium and ytterbium hydrides, whose properties are similar to those of the alkaline-earth compounds.

The lack of attention paid to these compounds is apparent. Thus, as recent work of Auphassorho[56] shows, even in the case of cerium, which has been most studied, new evidence has been obtained for the existence of a hydride of approximate composition CeH, with properties similar to those of the salt-like hydrides.

Since the reaction of most of the other rare-earth elements with hydrogen has been studied in even less detail than in the case of cerium, much new and interesting material should be obtained in further studies, particularly by physicochemical methods. Similarly the ability of these elements to form double boro- and aluminohydrides has so far received little attention. Further investigation of the individual properties of the rare-earth hydrides, double hydrides, and their derivatives appears promising, both as regards the appearance of individual characteristics in the separate members of the family and also as regards their practical applications.

CONCLUSION

Experiment shows that in rare-earth metal–hydrogen systems, compounds of constant composition and phases of intermediate composition exist in equilibrium. The solid phases MH_2–MH_3, which have been studied for cerium and lanthanum, are of particular interest in establishing the relationships observed in the transition between chemical compound and solution. In accordance with the views of Kurnakov on berthollide phases, there is in these phases a mobile equilibrium between several valency forms of the rare-earth metal. The experimental study of the composition and properties of the hydrides also reveals the individual features of the separate rare-earth metals, which on the whole resemble one another very closely.

Certain properties of the rare-earth hydrides, such as the thermal stability of the dihydrides and the change in the nature of the chemical bond in the MH_2–MH_3 range, indicate that it should be possible to use these compounds to advantage in special fields of metallurgy, certain types of synthesis by heterogeneous catalysis, and in the technology of semiconductor materials.

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THE CHEMISTRY OF QUINUCLIDINE DERIVATIVES

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