Stability of the Lanthanide Hydrides

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ABSTRACT

A review of the unclassified literature is presented that tabulates the reported equilibrium pressure data of the lanthanide diprotides and dideuterides in the form $\log P(\text{torr}) = A/T + B$. Values of the thermodynamic properties are tabulated and the trend in those data is explained by several semiempirical formulas. The isotope shifts are calculated by two independent means. For any lanthanide metal, the heat of formation of the dihydride is about 1.5 kcal/mole more negative than the dideuteride, which, in turn, is about 0.5 kcal/mole more negative than the ditritide. These values agree well with the experimental values.

I. INTRODUCTION

The hydrides of the lanthanide metals are among the most stable, and because of this stability they have potential applications in energy-related fields. It is time to look at the thermodynamic properties of the lanthanide dihydrides. Although all the lanthanide hydrides except EuH_2 react further to form trihydrides, they will not be discussed here.

Experimental data for the lanthanide diprotides, dideuterides, and in one case ditritide, are listed and discussed, relying heavily on previous reviews¹⁻⁴ and a computer search of the unclassified literature to April 1978. Several theoretical and semiempirical approaches are used to rationalize the observed trends in the thermodynamic properties and to predict the isotope shifts.

The electronic structures of EuH_2 and YbH_2 are significantly different from the others because of their half-filled (EuH_2) or filled (YbH_2) f-orbitals. This should lead to increased stability and, perhaps because of increased experimental difficulties, their

thermodynamic properties have not been reported. Data on the radioactive promethium have not been measured, but the remaining lanthanides are covered thoroughly in the literature. Data on scandium and yttrium are included here for comparison.

Reliable studies of the hydrides first appeared in the mid 1950s. Before that time, the pure metals were unavailable; therefore, all previous work is suspect. In the late 1950s and early 1960s, considerable work was done with the diprotides and dideuterides, previously reviewed by Mueller et al.,¹ Bos and Gayer,² and Beavis.³ Unfortunately, the important work of Jones et al.⁴ was overlooked.

II. SUMMARY OF THE DATA

The temperature variation of the equilibrium pressure of hydrogen over a lanthanide dihydride can be represented by the relationship¹

$$\log P (\text{torr}) = A/T + B \quad , \quad (1)$$

where A and B are constants and T is the absolute temperature. From the values of the two constants, estimates of the thermodynamic properties can be calculated from three relationships.

$$\Delta H^\circ = 2.303 RA , \quad (2)$$

$$\Delta S^\circ = R \ln 760 - 2.303 RB , \quad (3)$$

and

$$\Delta F^\circ = \Delta H^\circ - T\Delta S^\circ , \quad (4)$$

where ΔH° , ΔS° , and ΔF° are the standard enthalpy, entropy, and free energy of formation and R is the gas constant. These equations hold only for ideal, stoichiometric hydrides, which the lanthanide hydrides only approximate.

Table I summarizes the reported experimental data [A and B in Eq. (1)] for the lanthanide hydrides and deuterides and the values of the thermodynamic functions calculated from these constants. The experimental statistical error on A and B reported by most authors is not listed in this table. Several effects, such as impure samples, lack of equilibrium, systematic errors in temperature and pressure measurements, and isotopic impurities, can lead to errors in measurements. I believe that the reported statistical errors, generally 0.1 to 1%, are too optimistic and do not reflect reliably the data's accuracy. The data obtained for a given hydride by different authors usually fall outside the published errors.

Jones⁶ used a mass-spectrometric comparison technique to look at the differences between the equilibrium pressures of ErD_2 and ErT_2 . He found the ratio of the dideuteride pressure to the ditritide to be 0.91, continuing the stability trends seen in Table I.

Comparing the data in Table I, the work described in Refs. 7 and 5 appears more reliable. Korst and Warf⁷ studied lanthanum, cerium, praseodymium, and neodymium, and Jones et al.⁵ looked at yttrium, praseodymium, and the later elements terbium, dysprosium, holmium, erbium, thulium, and lutetium. In the following discussion, I give more consideration to the data of these authors because (1) their data appear more accurate when the whole data set is considered; (2) their values for praseodymium are in good agreement; and (3)

relative data for a series of elements done by a group of authors should be more reliable because the same techniques are used.

The various thermodynamic values calculated from the pressure data listed in Table I are plotted in Fig. 1 for the diprotides and in Fig. 2 for the dideuterides, where the two preferred sets of data are indicated with solid circles. The lines are drawn more to connect the points rather than to indicate the correct trend. However, a general trend seems evident. There is a gradual increase in all values as the atomic weight increases with a *definite* drop at lutetium and *probable* drop at gadolinium. This trend is discussed in the next section.

III. RELATIVE STABILITIES

No comprehensive theory of metal hydride stability has been proposed, primarily because of the wide variations in characteristics. A theoretical treatment of the lanthanide hydrides is particularly difficult because they are neither ionic nor covalent, but belong to the group of metallic hydrides. Nevertheless, several empirical and semiempirical treatments have been advanced and in this section they are applied to the set of data presented in the preceding section.

Mulford⁸ was the first to attempt to rationalize the variations in ΔH . He obtained approximately linear relationship by plotting the product of the molar volume of the hydride and its heat of formation against atomic number. Unfortunately, most of his reported data were estimated by an undisclosed thermodynamic method and it is difficult to judge the data's accuracy. He did predict that the stabilities should increase monotonically down the series, maximizing at erbium which is almost correct. Similarly, Magee⁹ plotted the free energy versus the room-temperature lattice parameter of the dihydrides, again obtaining an approximately linear plot. Scandium hydride did not fit the empirical curve, although yttrium did. Figure 3 shows a similar plot using the preferred set of data developed in the previous section. Note that except for lutetium, terbium, gadolinium (and scandium, which is well off the curve), a fairly regular trend maximizing at holmium and dysprosium is seen.

Magee⁹ also proposed plotting the free energy versus the ratio of metal-to-metal distance in the

TABLE I
EXPERIMENTAL THERMODYNAMIC PROPERTIES OF THE
LANTHANIDE HYDRIDES AND DEUTERIDES
 $\log_{10} P \text{ (torr)} = A/T + B$

Atomic Number	Element	Ref.	Hydride					Deuteride				
			-A	B	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta F^\circ$	-A	B	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta F^\circ$
21	Sc	4	9 050	9.17	41.4	28.8	33.6					
		13	10 490	10.48	48.0	34.8	38.5					
		3			47.8	34.9	38.3					
39	Y	14	11 870	10.52	54.3	35.0	44.8					
		15	9 710	8.80	44.4	27.1	37.0					
		5						11 300	10.15	51.7	33.3	42.6
57	La	16	10 860	10.76	49.7	36.1	39.9					
		7	10 850	10.64	49.7	35.5	40.0	10 170	10.11	46.5	33.1	37.5
		3			49.6	35.6	39.9			46.6	33.5	37.5
58	Ce	16	7 420	7.71	33.9	22.1	27.9					
		7	10 760	10.63	49.2	35.5	39.6	10 120	10.21	46.3	33.5	37.2
		17	12 000	11.90	54.9	41.3	43.6					
59	Pr	16	10 450	10.23	47.8	33.6	38.6					
		7	10 870	10.53	49.7	35.0	40.2					
		5	10 940	10.56	50.1	35.1	40.5	10 490	10.25	48.0	33.7	38.8
60	Nd	16	9 800	9.37	44.8	29.7	36.7					
		7	11 030	10.48	50.5	34.8	41.0					
61	Pm											
62	Sm	8	11 700	11.4	53.5	39.0	42.9					
63	Eu											
64	Gd	18	10 250	9.72	46.9	31.3	38.4					
65	Tb	5	11 320	10.38	51.8	34.3	42.4	10 840	10.24	49.6	33.7	40.4
66	Dy	5	12 120	11.16	55.5	37.9	45.1	11 410	10.54	52.2	35.1	42.6
67	Ho	5	12 120	11.10	55.5	37.6	45.2	11 630	10.93	53.2	36.8	43.2
		19	11 520	10.66	52.7	35.6	43.0	11 420	10.70	52.3	35.8	42.5
68	Er	20			52.6	35.2	43.0			52.9	35.8	43.1
		8	11 900	11.0	54.5	37.2	44.3					
		5	12 070	11.16	55.2	37.9	44.9	11 430	10.62	52.3	35.4	42.6
69	Tm	5	11 750	10.82	53.8	36.3	43.8	11 260	10.80	51.5	36.2	41.6
70	Yb											
71	Lu	5	10 730	10.20	49.1	33.5	40.0	10 340	9.78	47.3	31.6	38.7

Fig. 1.

Experimental values of ΔF° , ΔH° , and ΔS° for the formation of lanthanide diprotides.

Fig. 2.

Experimental values of ΔF° , ΔH° , and ΔS° for the formation of lanthanide dideuterides.

Fig. 3.

Variation of ΔF° versus the lattice parameter for the lanthanide diprotides.

pure metal to that in the hydride. He thought that as the metal-to-metal distance increased on hydriding, the metallic covalent cohesive bonding should decrease, thereby leading to decreased hydride stability. He again found that scandium did not fit the trends and suggested that perhaps there was a ratio giving maximum stability. Figure 4 shows such a plot for our set of data. Note that although there is a general increase in stability as the ratio approaches unity, gadolinium, scandium, lutetium, and yttrium again do not fit. None of these approaches suggests reasons for these variations. Also, because dideuterides have similar interatomic distances to the dihydrides, these methods do not explain the differences in the isotope stabilities.

A less empirical approach is through the use of the Born-Haber cycle and a calculated lattice energy.

Fig. 4.

Variation of ΔF° versus the ratio of the metal-to-metal distance in the pure lanthanide to that in the dihydride.

With this cycle, Gibb¹⁰ showed that the heat of formation of the dihydride is given by

$$\Delta H^\circ = U + S + D + I + 2E, \quad (5)$$

where S is the sublimation energy of the metal lanthanide, I is the sum of its first and second ionization potentials, D is the dissociation energy of the hydrogen molecule, and E is the electron affinity of the neutral hydrogen atom. U is the lattice energy, defined as the heat of the reaction

Gibb suggested using the Born-Landé equation

$$U = -330 A (1 - 1/n)/d_{MH}, \quad (7)$$

where A is the Madelung constant, d_{MH} is the metal-to-hydrogen distance, and n is an empirical constant, to calculate U . With this method, he estimated fairly reasonable values of U for ionic hydrides, although it failed with covalent hydrides, as expected.

Polyachenok and Novikov¹¹ followed this approach in studying the stabilities of the lanthanide dichlorides. They predicted and observed a trend analogous to that seen above for the hydrides with

sharp drops in the stability curves at gadolinium and lutetium. The results of these calculations for the lanthanide dihydrides are presented in Table II, using the ionization potentials suggested by Polyachenok and Novikov. Although the results compare poorly with the experimental values, similar trends are seen in the calculated ΔH° . As seen in Table II, the drops in the middle and end of the series can be attributed directly to the changes in S , the heat of sublimation. Thus it seems probable that the discontinuities in the measured ΔH° values can be traced to the variations in S .

IV. ISOTOPIC SHIFTS

Although the lattice energy approach failed to predict quantitatively the differences seen across the lanthanide series, the method should be more successful in predicting the smaller isotope shift. As indicated by Eq. (5), because S and I are characteristic of the metal only, they would not change if the hydrogen isotope were changed. Also, the electron affinity should be the same for the three hydrogen isotopes because it is a property of the electronic orbitals only. Therefore, only the lattice energy U and the dissociation energy D should be effective in

TABLE II

BORN-HABER CALCULATIONS OF THE LANTHANIDE DIHYDRIDES

M	d_{MH}	$-U^a$	$2E+D$	S	I		ΔH°
					Exp	Est	
La	2.83	525	+73	97	391	390	+35
Ce	2.79	533	+73	96		390	+26
Pr	2.76	539	+73	78	382	390	+2.3
Nd	2.73	544	+73	76	386	390	-5
Pm	2.71	548	+73	62		390	-24
Sm	2.69	553	+73	50	391	390	-40
Eu	2.67	557	+73	42	389	390	-52
Gd	2.65	560	+73	84		420	32
Tb	2.62	567	+73	87		420	29
Dy	2.60	572	+73	62		420	-1
Ho	2.58	577	+73	70		420	+2
Er	2.56	581	+73	66		420	-6
Tm	2.55	583	+73	58		420	-16
Yb	2.53	588	+73	40	423	420	-39
Lu	2.52	590	+73	95		420	14

^a $U = -330 (5.04)/d_{MH} [1 - 1/9.5]$.

calculating the isotope shift. Generally, the lattice parameter of the protides is about 0.2% greater than that of the deuterides. From this difference, Eq. (7) indicates that U should be about 0.5 kcal/mole more negative for LnD_2 than for LnH_2 . But the dissociation energy of D_2 is 2 kcal/mole greater (more positive) than for H_2 . The result is that ΔH° for LnD_2 should be about 1.5 kcal/mole less negative than ΔH° for LnH_2 for all the lanthanide metals. Table I shows that the dideuteride is always less stable than the diprotide by 1 to 3 kcal/mole, which agrees with the theory.

For the tritide-to-deuteride comparison, the lattice parameter should change even less, and the dissociation energy of tritium is about 0.8 kcal/mole more positive than for deuterium. Therefore, the tritide should be slightly less stable than the deuteride, but the differences will be smaller than for the deuteride and protide. These calculations neglect the zero-point energy, which is discussed below.

Another approach to calculating the isotope shift is through statistical mechanics. In his approach to palladium hydride, Lacher¹² showed that for exothermic absorbers in which M_a hydrogen atoms are arranged in N_a available sites, the energy of a given hydrogen atom is given by

$$E = -M_a W_H - 1/2 M_a^2 W_{HH} / N_a, \quad (8)$$

where W_H is the energy of the atom in its site and W_{HH} is the interaction energy between different hydrogen atoms. From this assumption Lacher was able to show that the pressure within the plateau region could be expressed by

$$\ln P^{1/2} = -(1/2 W_{HH} + W_H - 1/2 D) / kT + \ln[(KTF_2)^{1/2} / v(T)], \quad (9)$$

where D is again the dissociation energy of the hydrogen molecule, F_2 is related to the partition function of the gaseous hydrogen molecule, and $v(T)$ is the partition function of the hydrogen atom in its site. If we now assume that the last logarithmic function is independent of temperature (which it is only approximately), then the heat of formation can be associated with the first term on the right-hand

side of Eq. (9). Then by comparison with Eqs. (1) and (2),

$$\Delta H^\circ = -W_{HH} - 2W_H + D. \quad (10)$$

W_H is the zero point energy and, if we assume the hydrogen atom behaves as an isotropic oscillator, this is given by $W_H = -3/2 h\nu$, where ν is its vibrational frequency. Further, because $\nu_D = \nu_H(m_H/m_D)^{1/2}$, we can calculate this difference if we know one of the frequencies. As an estimate, we take $\nu_H = 10^{13} \text{ s}^{-1}$, which leads to $W_H - W_D = -400 \text{ kcal/mole}$ and $W_T - W_D = -200 \text{ kcal/mole}$.

Lacher showed that $W_{HH} = 4kT_C$ where T_C is the critical temperature of the hydride; that is, the temperature above which the two-phase system becomes one. This has not been measured for the lanthanides, therefore we must assume they are the same for all three isotopes. From these assumptions and Eq. (10) we can then calculate that $\Delta H_H^\circ - \Delta H_D^\circ = -1.2 \text{ kcal/mole}$ and $\Delta H_T^\circ - \Delta H_D^\circ = -0.4 \text{ kcal/mole}$ for all the lanthanides, which agrees with the last calculations.

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