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Thermodynamics of the Lanthanum–Hydrogen System at 917°K

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The binary system lanthanum–hydrogen has been studied at pressures up to 1 atm at 917°K by a calorimetric–equilibrium method. From the calorimetric measurements we found the enthalpy of formation of LaH_2 at 917°K to be -45.7 kcal mole^{-1} with an estimated uncertainty at ± 0.3 kcal mole^{-1}. This result is about 4 kcal mole^{-1} less negative than the values derived indirectly from plateau pressure equilibrium measurements by Mulford and Halley and by Korst and Warf. A comparison between the calorimetric and equilibrium measurements at 917°K provides information on the partial entropy of hydrogen in lanthanum and in the dihydride $LaH_{2\pm\delta}$. The excess entropy of hydrogen in lanthanum is about 6 cal K^{-1} mole^{-1} at 917°K: this value is essentially fully accounted for by the estimated vibrational entropy contribution of the hydrogen atoms. In $LaH_{2\pm\delta}$ the partial entropy of hydrogen changes from small negative values at $X \approx 1.95$ to positive values for $X > 2$. This entropy change is explained by an assumed intrinsic disorder of hydrogen in LaH_2 of about 0.02.

Introduction

The early investigations of rare earth–hydrogen systems originated with the work of Winkler in 1891. Of course, all early studies in this field must be viewed with some scepticism due to the difficulty of separating one rare earth metal from another. Investigations up to 1960–1965 were reviewed by Mikheeva and Kost (*1*), by Libowitz (*2*), and by Bos and Gayer (*3*). In the postwar years detailed thermodynamic investigations of pure rare earth–hydrogen systems were initiated by Mulford and Holley (*4*) in 1955, followed by Korst and Warf (*5*) in 1966. For hydrogen–lanthanum ratios larger than 2 there also are equilibrium studies by Hardcastle and Warf (*6*) and by Messer and Hung (*7*).

While the heats of formation of some rare earth hydrides of somewhat uncertain metal composition were measured by acid solution calorimetry by Sieverts and Gotta (*8*), there have so far been no direct calorimetric determinations of the enthalpy of formation of rare earth hydrides. Generally enthalpy data quoted in the literature have been calculated from the temperature dependence of the hydrogen plateau pressures in the temperature range 700–1200°K. For lanthanum–hydrogen such data were reported in the quoted papers by Mulford and Holley (*4*) and by Korst and Warf (*5*).

During recent years there has been increasing interest in the possibility of applying rare earth metals for energy storage (*9*) and for various metallurgical purposes (*10*)

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(see, e.g., reviews by Raman (*10, 11*)). Apart from these considerations the present investigation was initiated in order to obtain direct calorimetric–equilibrium data for a metal–hydrogen system which has a dihydride with an extensive range of homogeneity, both below and above MH_2. The measurements reported below were carried out at 917°K using an apparatus which has been described previously (*12*).

In equilibrium studies the formation of $LaH_2(s)$ from $La(s) + H_2(g)$ involves the reaction

$$\frac{2}{2-\delta-X}\,LaH_X(s) + H_2(g) = \frac{2}{2-\delta-X}\,LaH_{2-\delta}(s). \quad (1)$$

In this expression X is the solubility of hydrogen in lanthanum, while δ is the "solubility" of vacancies in LaH_2. For small values of X and δ we will have

$$\Delta\bar{G}_f^\circ \approx RT \ln p_{H_2}$$

and

$$\Delta\bar{H}_f^\circ \approx \partial\left(\frac{\partial G_f^\circ}{T}\right)\Big/\partial\left(\frac{1}{T}\right).$$

Clearly the Gibbs energy and enthalpy changes associated with Eq. (1) can be equated with the "true" formation data only if $X \rightarrow 0$ and $\delta \rightarrow 0$. For the lanthanum–hydrogen system the values of X and δ in the reported equilibrium studies were of the order of 0.1. Thus it is difficult to estimate to what extent the published data differ from the "true" values.

Experimental and Materials

In the present investigation our standard vacuum line gas-measuring assembly was connected to a single-unit Calvet-type high-temperature microcalorimeter (*13, 14*). The calibration of the calorimeter involved electrical measurements checked by a drop method. Since, to some extent, heat generated in the calibration heater leaks by conduction along the axis of the calorimeter (through lead wires, stainless-steel and silica liners, etc.), all calibrations were based on the drop data. For this purpose we constructed a special fused silica liner which allowed weighed pieces of platinum to be dropped into the calorimeter from room temperature within a hydrogen atmosphere. In other respects the calibration assembly reproduced the experimental conditions which applied during the metal–hydrogen absorption experiments. During the experimental runs electrical calibrations were performed every day, while comparisons between the electrical calibrations and the drop calibrations were carried out before and after each separate series of measurements.

The hydrogen gas was purified by absorption in and desorption from titanium powder. The lanthanum metal was obtained from Nuclear Corporation of America and had a nominal purity of 99.9% La. The metal was available in 1-in.-diameter ingot form; small-size chips were machined from this ingot on a carefully cleaned lathe. The turnings were cleaned in tetrachlorethylene and absolute alcohol, and then stored *in vacuo;* all subsequent operations were carried out in a dry box.

Before each series of measurements the lanthanum sample was first annealed at 850°K and then treated with hydrogen gas of 1 atm pressure at 950°K. After 48 hr at this temperature the hydrogen was removed *in vacuo* of 10^{-6} Torr. In order to avoid possible cumulative oxygen contamination, a new lanthanum sample was used for each series of measurements.

At room temperature lanthanum has a close-packed hexagonal structure with $c/a = 1.613$. Near 565°K the metal transforms to the fcc form, which was the modification involved in our measurements at 917°K.

Results. Comparison with Earlier Work

Partial Gibbs Energies of Hydrogen

Under the conditions of our measurements we found that the initial uptake of hydrogen by the pure metal was very fast; for samples within the LaH_X solid solution region equilibrium was reestablished about 25 min after each addition of gas ($\sim 3 \times 10^{-4}$ mole of H_2). In the dihydride phase attainment of equilibrium typically required a somewhat longer time, about 35–40 min.

The LaH_X solid solution range. In Fig. 1 we have plotted our equilibrium pressures according to Sievert's equation (*15*)

$$X/p^{1/2} = a + bp^{1/2} \qquad (p \text{ in Torr}). \quad (2)$$

The average of the two series of measurements is well represented by this expression with the coefficients $a = 0.03 \pm 0.01$ and $b = 1.7 \pm 0.15$.

The two-phase region, $LaH_X(s) + LaH_2(s)$. In the two-phase region we observed a constant equilibrium pressure of 0.074 Torr. From this value combined with Eq. (2) we found the limiting value of X in LaH_X to be 0.13 ± 0.01.

In the earlier studies of the lanthanum–hydrogen system by Mulford and Holley (M&H), and by Korst and Warf (K&W), the equilibrium pressures in the two-phase region were expressed by

$$\log p(\text{Torr}) = 10.758 - 10858/T \text{ (M\&H)}$$

and

$$\log p(\text{Torr}) = 10.644 - 10847/T \text{ (K\&W)}.$$

From these expressions we calculate at 917°K, $p = 0.065$ Torr (K&W) and 0.083 Torr (M&H), respectively. Thus our own value falls at the mean of the two earlier values.

The $LaH_{2\pm\delta}$ hydride phase. At the end of the $LaH_X(s) + LaH_{2-\delta}(s)$ two-phase region there is a very steep increase in the equilibrium pressures. This is well illustrated in Fig. 2a which shows a plot of log p against composition. From the data shown in this figure we estimated that the limit of the two-phase region at 917°K is $X = 1.90 \pm 0.03$ (i.e., $\delta = 0.1 \pm 0.03$). This value is not in entirely satisfactory agreement with that of Korst and Warf who found that the limit of the two-phase region at 929°K occurs near $X = 1.8$ (± 0.05?).

Libowitz (*2, 16*) has discussed nonstoichiometry and lattice defects in rare earth hydrides with small deviations from stoichiometry. From his work we find that the value of $(\partial \ln p/\partial X)_T$ at $\delta = 0$ should equal α^{-1}, the inverse of the intrinsic disorder in the hydride (see below). From our plot of log p against X in Fig. 2 we find (∂ log

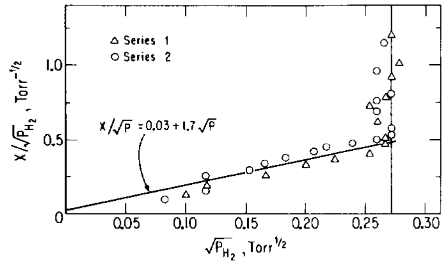

FIG. 1. Plot of $X/p_{H_2}^{1/2}$ against $p_{H_2}^{1/2}$ for solutions of hydrogen in lanthanum at 917°K.

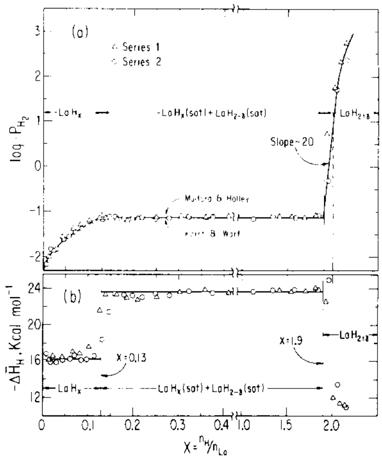

FIG. 2. (a) Plot of log p_{H_2} against composition for hydrogen in the lanthanum–hydrogen system at 917°K. (b) Plot of $\Delta\bar{H}_H$.

$p/\partial X) \approx 20$, i.e., $\alpha \approx 0.022$ at 917°K. This is in very acceptable agreement with the value given by Libowitz for LaH_2 at 700°C, $\alpha \approx 0.05$.

Partial Enthalpies of Hydrogen

Letoquart *et al.* (*17*), and independently Boureau and Kleppa (*18*), have shown that in gas–solid calorimetric measurements the corrected partial molar enthalpy of hydrogen may be obtained from the expression

$$\Delta\bar{H}_{\mathrm{H}} = \frac{q}{\delta n_{\mathrm{H}}} - V\frac{\delta p}{\delta n_{\mathrm{H}}}, \qquad (3)$$

where q is the observed heat, V is the effective volume of the calorimeter, δp is the pressure increase in the experiment, and δn_{H} is the number of moles of hydrogen atoms which are brought to reaction with the solid sample. In the present study the term $V(\delta p/\delta n_{\mathrm{H}})$ was estimated to represent 0.3% or less of the observed heat effects. Since this term fell well within the experimental scatter, it has been neglected in the evaluation of the data. Our partial enthalpies are shown graphically in Fig. 2b.

The LaH_X solid solution. The most reliable enthalpy values in this range of compositions were obtained in Series 2, which yielded $\Delta\bar{H}_{\mathrm{H}} = -16.3 \pm 0.3$ kcal mole^{-1} H. Within experimental error we found no dependence of $\Delta\bar{H}_{\mathrm{H}}$ on composition.

The two-phase region, $LaH_X(s) + LaH_{2-\delta}(s)$. Except for a small seemingly reproducible drop in the measured enthalpies near $X = 0.2$, $\Delta\bar{H}_{\mathrm{H}}$ was found to be constant throughout the two-phase region. The average value was -23.6 ± 0.3 kcal mole^{-1} H.

This result may be compared with corresponding partial enthalpies derived in the equilibrium studies of Mulford and Holley (-24.85 kcal mole^{-1} H) and Korst and Warf (-24.8 kcal mole^{-1} H). The latter authors also measured $\Delta\bar{H}_{\mathrm{D}}$ for $LaD_X(s) + LaD_{2-\delta}(s)$ and found -23.25 kcal mole^{-1} D, i.e., 1.55 kcal larger than for $\Delta\bar{H}_{\mathrm{H}}$. This difference is too large to be explained by the isotope effect. Note that our own value of $\Delta\bar{H}_{\mathrm{H}}$ falls closer to their $\Delta\bar{H}_{\mathrm{D}}$ than to $\Delta\bar{H}_{\mathrm{H}}$.

ΔH°_{f} for LaH_2 at 917°K. From our calorimetric data we have derived the heat of formation, ΔH°_{f}, for LaH_2 in two different ways:

(a) By summing all the actually measured experimental heat effects we have

$$\Delta H^{\circ}_{f}\,(\text{per mole } LaH_2) = 2^{\circ}_{f}\frac{\Sigma q_{\mathrm{i}}}{\Sigma \delta n_{\mathrm{H}}}.$$

For our Series 1, this summation yields

$\Delta H^{\circ}_{f}(917) = -45.55$ kcal mole^{-1};

for Series 2,

$\Delta H^{\circ}_{f} = -45.64$ kcal mole^{-1}.

(b) We also carried out the following integration

$$\Delta H^{\circ}_{f} = \int_0^2 \Delta\bar{H}_{\mathrm{H}}(X)dx$$

$$\text{where } X = \frac{n_{\mathrm{H}}}{n_{\mathrm{La}}}. \qquad (4)$$

In this integration we adopt the following values of $\Delta\bar{H}_{\mathrm{H}}$ for the indicated ranges of composition:

Solid phase	Composition range ($X = n_{\mathrm{H}}/n_{\mathrm{La}}$)	$\Delta\bar{H}_{\mathrm{H}}$ (kcal mole^{-1} H)
$La–LaH_X$	$0 < X < 0.13$	-16.3 ± 0.3
$LaH_X(s) + LaH_{2-\delta}(s)$	$0.13 < X < 1.9$	-23.6 ± 0.3
$LaH_{2-\delta}–LaH_2$	$1.9 < X < 2.0$	$\int_{1.9}^{2.0} \Delta\bar{H}_x dx = -1.8$

On this basis we found ΔH_f° of LaH_2 at 917°K to be −45.7 kcal mole^{-1}, with an estimated uncertainty of ±0.3 kcal mole^{-1}, in very good agreement with the values obtained by direct summation. Again our results are in less satisfactory agreement with the values derived from the plateau pressure equilibrium measurements, namely, −49.7 ± 0.1 kcal mole^{-1} (Mulford and Holley) and −49.6 ± 1.0 (Korst and Warf). However, strictly speaking these earlier enthalpy values refer to the process expressed by Eq. (1) rather than to $La(s) + H_2(g) = LaH_2(s)$. Somewhat better agreement with the present data is obtained if we combine the earlier equilibrium values of $\Delta\bar{H}_H$ with our own calorimetric results for the two single-phase regions; this yields $\Delta H_f^\circ = -47.8$ kcal mole^{-1} for LaH_2, still about 5% more exothermic than the calorimetric value.

The Partial Entropies of Hydrogen: Discussion

By combining $\Delta\bar{G}_H = \frac{1}{2} RT \ln p_{H_2}$ and $\Delta\bar{H}_H$ we may calculate the corresponding values of the relative partial molar entropy, $\Delta\bar{S}_H$, referred to one-half mole of hydrogen gas of 1 atm pressure. We shall consider separately the partial entropies of hydrogen in the LaH_X solid solutions and in the $LaH_{2\pm\delta}$ hydride phase.

The LaH_X solid solution. If we adopt the value 19.54 cal K^{-1} mole^{-1} for $\frac{1}{2}\, S^\circ_{H_2}$ at 917°K (*19*) we can calculate the partial molar entropy of hydrogen atoms in the lanthanum–hydrogen solid solution from the expression

$$\bar{S}_H = \Delta\bar{S}_H + 19.54 \qquad (5a)$$

and the *excess* partial molar entropy from

$$\bar{S}^E_H = \bar{S}_H + R \ln \frac{X}{1 - X}. \qquad (5b)$$

The latter expression arbitrarily defines the ideal configurational partial entropy on the basis of one interstitial site per solvent metal atom; it is assumed that the hydrogen atoms are distributed randomly among these sites. The experimental values of $\bar{S}_H$ and $\bar{S}^E_H$ at 917°K are shown in Fig. 3. Within our experimental error we found no dependence of $\bar{S}^E_H$ on composition. For Series 2 we found the average value of $\bar{S}^E_H$ to be 6 cal K^{-1} mole^{-1} H.

To the best of our knowledge there are, as yet, no inelastic neutron scattering data which provide direct information on the vibrational frequency of hydrogen in lanthanum–hydrogen solid solutions. On the other hand, from the neutron scattering work of Hunt and Ross (*20*) it is known that the optical vibrations of hydrogen in the nonstoichiometric dihydride $LaH_{1.94}$ lie in a band of about 200-cm^{-1} width which is centered near 830 cm^{-1}.

From the equilibrium data of Korst and Warf it is possible to make an independent estimate of $\bar{\nu}_H$. Using their plateau pressures in the lanthanum–hydrogen and lanthanum–deuterium systems we calculate at 917°K

$$\Delta\bar{G}_D - \Delta\bar{G}_H = \frac{1}{2} RT \ln(p_{D_2}/p_{H_2})$$
$$= 420 \text{ cal mole}^{-1}.$$

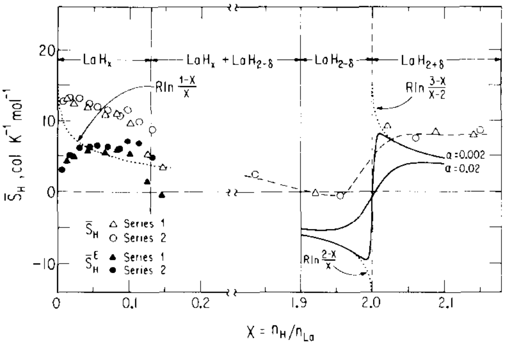

FIG. 3. Plot of the partial entropy of hydrogen against composition in the lanthanum–hydrogen system at 917°K. The curves denoted $R \ln[(1 - X)/X]$, $R \ln[(2 - X)/X]$, and $R \ln[(3 - X)/(X - 2)]$ refer to idealized models (see text). The curves denoted $\alpha = 0.02$ and $\alpha = 0.002$ have been calculated from a nearly ordered model for $LaH_{2\pm\delta}$ discussed in the text (α = intrinsic disorder).

If we adopt the simple harmonic oscillator model and set $\nu_H = \nu_D 2^{1/2}$, we calculate from this difference $\tilde{\nu}_H = 738\ cm^{-1}$. This result may be compared with the neutron scattering value for $\tilde{\nu}_H$ in fcc palladium, 552 cm^{-1}, according to Drexel *et al.* (*21*).

It may perhaps be argued that the value $\tilde{\nu}_H = 738\ cm^{-1}$, since it was derived from the plateau pressures, actually represents the vibrational frequency of hydrogen in the dihydride. On the other hand, it may be argued with equal validity that the value reflects the frequencies in the saturated LaH_X and LaD_X solid solutions.

Quite recently Boureau *et al.* (*22*) have shown that vibrational frequencies for hydrogen in metals calculated from the isotope effect tend to yield too large values for $\tilde{\nu}_H$; for hydrogen in palladium such calculations yield frequencies which are 10–15% too large compared to the neutron scattering value. Since the calculated $\tilde{\nu}_H$ is in fact *lower* than the reported neutron scattering value for $LaH_{1.94}$, it seems likely that the second of the above interpretations is closer to the truth.

On this basis we have assumed, with Boureau *et al.* (*22*), that the quoted calculated value is somewhat too large and have set $\tilde{\nu}_H \cong 650\ cm^{-1}$. This estimate seems quite plausible in view of the somewhat larger value found by Hunt and Ross for hydrogen in $LaH_{1.94}$.

If we adopt this value of $\tilde{\nu}_H$ we calculate the vibrational entropy of hydrogen in lanthanum to be 6.15 cal K^{-1} $mole^{-1}$ at 917°K. This estimate differs little from our experimental value of $\bar{S}_H^E$, and suggests that the excess entropy of hydrogen in lanthanum may perhaps be fully accounted for by the vibrational contribution. If this is indeed the case, it would imply that other entropy terms such as, e.g., those arising from a possible modification of the vibrational spectrum of lanthanum (i.e., from a change in Debye θ) and from the change in the electronic density of states (i.e., from $\partial\gamma/\partial X$), either are quite small or tend to cancel.

We are not aware of low-temperature heat capacity data for LaH_X that might throw further light on this question. In fact, even if such data were available, they would apply to cphex lanthanum rather than to the fcc modification.

The $LaH_{2\pm\delta}$ hydride phase. Lanthanum dihydride has the CaF_2 (fluorite) structure. In the fully ordered form of this hydride the lanthanum atoms occupy fcc sites while the two hydrogen atoms completely fill all available tetrahedral interstitial sites (T sites).

It is well known that many metal dihydrides exhibit significant deviations from stoichiometry (*2*). The most common type of nonstoichiometry is due to vacancies in the T-site (hydrogen) sublattice. We showed above that for lanthanum dihydride at 917°K this nonstoichiometric region extends to about $LaH_{1.9}$.

In some metal–hydrogen systems, particularly among the rare earths, it is also possible to realize dihydride compositions with hydrogen/metal ratios which are significantly larger than 2. In this case hydrogen atoms also occupy octahedral interstitial sites (O sites) in the close-packed array of metal atoms. Lanthanum dihydride provides a good example of such behavior; we have in the present work carried out calorimetric–equilibrium measurements on this hydride up to the composition $LaH_{2.15}$.

In nonstoichiometric dihydrides which become fully ordered at the stoichiometric composition, the ideal configurational partial entropies of hydrogen can easily be calculated:

(a) For $X < 2$, if the vacancies are distributed randomly among the $2N$ interstitial T sites (two sites per metal atom), we have $\bar{S}_H(\mathrm{conf}) = R \ln [(2 - X)/X]$; this will approach $-\infty$ as $X \rightarrow 2$.

(b) For $X > 2$, if excess hydrogen atoms are distributed randomly among the N interstitial O sites (one site per atom), we have $\bar{S}_H(\text{conf}) = R \ln [(3 - X)/(X - 2)]$. This will approach $+\infty$ as $X \rightarrow 2$.

In the real world this idealized picture is of course never realized. Since the energy difference between T and O sites is finite, there will always be some occupancy of O sites before the T-site sublattice is completely filled. Conversely, if we approach the stoichiometric composition from $X > 2$, some vacancies will be created in the T-site sublattice before the concentration of hydrogen in the O sites reaches zero.

For lanthanum dihydride this type of behavior was noted some 15 years ago by Schreiber and Cotts (*23*). These authors found a strongly concentration-dependent line narrowing of their NMR signals in LaH_X for $X > 1.92$; they suggested that this was due to some filling of the octahedral sites. Very recently Weaver *et al.* (*24*) and Peterman *et al.* (*25*) reached very similar conclusions when they considered the influence of hydrogen sublattice concentration on the optical properties and the electronic band structure of some rare earth dihydrides.

The thermodynamic properties of lanthanum dihydride may conveniently be discussed in terms of the statistical theory of solutions with substantially ordered atomic distributions as originally developed by Wagner and Schottky (*26*) and by Ölander (*27*). More recent summaries of these theories are given by Wagner (*28*, *29*). The already quoted studies of the rare earth hydrides by Libowitz (*2*, *16*) are closely related.

In the following we shall calculate the partial configurational entropy of hydrogen in the dihydride in terms of the intrinsic disorder α. Libowitz (*2*) concluded that the intrinsic disorder in LaH_2 at 700°C is about 5%, i.e., that at $X = 2.0$ 5% of the O sites are occupied by hydrogen while at the same time 2.5% of the T sites are vacant.

Formally we may express the disordering reaction in lanthanum dihydride by

$$H_T \rightleftarrows V_H + H_i. \tag{6}$$

Here H_T represents an H atom on a normal T site, V_H represents hydrogen vacancies in the T-site sublattice, while H_i represents hydrogen interstitials on the O sites. We shall make use of the following quantities:

$$X = n_H/N,$$
$$X_v = n_v/2N,$$
$$X_i = n_i/N.$$

Here

n_H = total number of hydrogen atoms,
n_v = number of vacancies in T-site sublattice,
n_i = number of hydrogen atoms in O-site sublattice,
N = number of lanthanum atoms.

We have

$$\delta = X_i - 2X_v. \tag{7}$$

For $X \gtreqless 2$, we have $\delta \gtreqless 0$. With Wagner (*28*) and Libowitz (*2*) we define the intrinsic disorder, α, through the relation

$$\alpha^2 = 2X_iX_v. \tag{8}$$

Let us neglect all interactions between the various defects and assume that these are randomly distributed. For simplicity we shall also assume that $n_v \ll N$ and $n_i \ll N$. If the n_v vacancies are distributed over the $2N$ T sites and the n_i interstitial atoms over the N O sites, we can write for the number of complexions

$$\Omega = \frac{2N!}{n_v!(2N - n_v)!} \cdot \frac{N!}{n_i!(N - n_i)!}.$$

From this we obtain by Stirling's approximation

$$\begin{aligned} S_{\text{conf}} &= k \ln \Omega \\ &= -R[2(\ln(1 - X_v) + X_v \ln X_v) \\ &\qquad + \ln(1 - X_i) + X_i \ln X_i]. \end{aligned} \tag{9}$$

Using the fact that $X_v \ll 1$ and $X_i \ll 1$ we also have

$$S_{\mathrm{conf}} \approx R[2X_v(1 - \ln X_v) + X_i(1 - \ln X_i)]. \quad (10)$$

From (7) and (8) above we get

$$X_i = \frac{\delta + (\delta^2 + 4\alpha^2)^{1/2}}{2} \quad \text{and} \quad X_v = \frac{-\delta + (\delta^2 + 4\alpha^2)^{1/2}}{4}. \quad (11)$$

Thus also

$$S_{\mathrm{conf}} = R\left[\frac{-\delta + (\delta^2 + 4\alpha^2)^{1/2}}{2}\left(1 - \ln\frac{-\delta + (\delta^2 + 4\alpha^2)^{1/2}}{4}\right) + \frac{\delta + (\delta^2 + 4\alpha^2)^{1/2}}{2}\left(1 - \ln\frac{\delta + (\delta^2 + 4\alpha^2)^{1/2}}{2}\right)\right]. \quad (12)$$

Since $\bar{S}_{\mathrm{H}} = \partial S/\partial n_{\mathrm{H}}$, and with $dn_{\mathrm{H}} = d\delta$, we get

$$\bar{S}_{\mathrm{H,conf}} = \frac{R}{2}\left[(1 - \delta(\delta^2 + 4\alpha^2)^{1/2})\ln\frac{-\delta + (\delta^2 + 4\alpha^2)^{1/2}}{4} - (1 + \delta(\delta^2 + 4\alpha^2)^{-1/2})\ln\frac{\delta + (\delta^2 + 4\alpha^2)^{1/2}}{2}\right]. \quad (13)$$

This expression applies for both positive and negative values of δ, i.e., for $X \gtreqless 2$.

We have in Fig. 3 included calculated curves for $\bar{S}_{\mathrm{H,conf}}$ for $\alpha = 0.02$ and 0.002. Note that the observed partial entropies of hydrogen are about 4–5 cal K^{-1} mole^{-1} more positive than the calculated curve for $\alpha = 0.02$. This difference undoubtedly is largely due to the vibrational entropy of hydrogen which, from the neutron scattering frequency of Hunt and Ross, is estimated to be 4.8 cal K^{-1} mole^{-1} at 917°K.

From Fig. 3 we see that the observed partial entropy, $\bar{S}_{\mathrm{H}}$, for $\mathrm{La}_{2+\delta}$ with $\delta \gtrsim 0.1$ seems to level off at about 8 cal K^{-1} mole^{-1} H at 917°K. This result may be compared with $\bar{S}_{\mathrm{H}} = -13.0 + \frac{1}{2}S^{\circ}_{\mathrm{H}_2}$ (350°C) $= -13.0 + 18.2 = 5.2$ cal K^{-1} mole^{-1} H calculated from the data of Messer and Hung (7) for $\mathrm{LaH}_{2.2}$ near 350°C. A major part of the difference between these two values can be accounted for by the vibrational heat capacity of hydrogen.

Acknowledgments

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