On extending Miedema's model to predict hydrogen content in binary and ternary hydrides

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Abstract

While originally formulated to predict the enthalpy of formation, Miedema's model for metal hydrides is also capable of predicting hydrogen content. In the case of binary AH_x hydrides this is straightforward. For ternary AB_nH_x hydrides extension of the model to arbitrary hydrogen content x is required. An *ansatz* for doing so is proposed which also extends the model to arbitrary B:A ratio n while preserving Miedema's original prescription for $n = 1, 2, 3, 5$. Results are reported for all known solid binary hydrides and for a variety of ternary systems. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Miedema and co-workers developed a very successful model for the enthalpy of formation ΔH of binary intermetallic alloys with a primary focus on materials in which at least one of the elements is a transition metal (TM). Detailed description of the method can be found in Ref. [1]. The model was broadened to include binary [2] and ternary [2–5] TM hydrides of known hydrogen concentration. Here it is pointed out that the model can also predict hydrogen content. Such predictions can be obtained for binary AH_x hydrides in a straightforward way within the form of the model. For ternary AB_nH_x hydrides, however, extension of the model to arbitrary hydrogen content x is required. An *ansatz* for doing so is proposed which also extends the model to arbitrary B:A ratio n while preserving Miedema's original restriction to hydrides characterized by $n = 1, 2, 3, 5$.

2. Binary hydrides

In general Miedema's expression for the enthalpy of formation of a binary $A_{c_A}B_{c_B}$ alloy is

$$\Delta H(A_{c_A}B_{c_B}) \equiv \Delta H'(A_{c_A}B_{c_B}) + c_A \, \Delta H_{trans}(A) + c_B \, \Delta H_{trans}(B) \tag{1}$$

$\Delta H'(A_{c_A}B_{c_B})$ is constructed assuming the elements A and B are both metals:

$$\Delta H'(A_{c_A}B_{c_B}) = fgP \left[-(\Delta \phi^*)^2 + \frac{Q}{P}(\Delta n_{WS}^{1/3})^2 - \frac{R}{P} \right] \tag{2}$$

The components of Eq. (2) are

$$\Delta \phi^* = \phi_A^* - \phi_B^* \tag{3a}$$

$$\Delta n_{WS}^{1/3} = (n_{WS}^A)^{1/3} - (n_{WS}^B)^{1/3} \tag{3b}$$

$$f = c_A^s c_B^s [1 + 8(c_A^s c_B^s)^2] \tag{3c}$$

$$g = \frac{2}{(n_{WS}^A)^{-1/3} + (n_{WS}^B)^{-1/3}} \tag{3d}$$

$$c_i^s = \frac{c_i(V_i^{alloy})^{2/3}}{c_A(V_A^{alloy})^{2/3} + c_B(V_B^{alloy})^{2/3}} \tag{3e}$$

and

$$(V_i^{alloy})^{2/3} = V_i^{2/3} \left[1 + a\frac{f}{c_i^s}(\phi_i^* - \phi_j^*) \right] \tag{3f}$$

Here i and j denote A or B; the ϕ_i^* are effective chemical potentials; n_{WS}^i is the electron density at the boundary of the Wigner–Seitz cell of parent metal i; V_i is the molar

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volume of i while c_i and V_i^{alloy} are, respectively, its concentration and volume in the alloy; and the c_i^s are effective surface concentrations (V_i^{alloy} and c_i^s are inter-dependent, so they must be computed self-consistently). A $\Delta H_{\text{trans}}(i)$ term on the right side of Eq. (1) only appears if element i is non-metallic; $\Delta H_{\text{trans}}(i)$ represents the energy to transform element i from its actual ground state to a metal. In the case of hydrogen, for example, Miedema and co-workers [1,2] estimated $\Delta H_{\text{trans}}(H) = 100$ kJ/mol H for the energy to transform H_2 gas to metallic hydrogen.

Miedema employed the experimentally determined compositions in performing calculations with the model for hydrides. The primary objective was to obtain theoretical values for enthalpies of formation. The model can be examined in a different, perhaps even more stringent, way, however, by also deriving its prediction for the hydrogen content. For a binary hydride AH_x this is straightforward, requiring only the evaluation of Eq. (1) over a range of x to find the minimum in $\Delta H(AH_x)$, expressed in terms of energy per AH_x formula unit:

$$\Delta H(AH_x) = (1 + x)\, \Delta H(A_{1/(1+x)}H_{x/(1+x)}) \qquad (4)$$

The minimum $\Delta H(AH_x)$ is the enthalpy of formation of the most stable hydride which forms when element A reacts with hydrogen gas:

$$A + \frac{1}{2}xH_2 \rightarrow AH_x \qquad (5)$$

$\Delta H(AH_x)$ can also be interpreted as the negative of the corresponding heat of reaction. In general Miedema's model produces at most one minimum for any given hydride.

Table 1 and Figs. 1 and 2 contain results for all solid binary hydrides AH_x for which experimental information exists and model parameters [1] are available. In the figures x_{calc} is the hydrogen content x minimizing $\Delta H(AH_x)$, and x_{expt} is the observed value. Table 1 lists these quantities as well as the corresponding enthalpies of formation $\Delta H_{\text{calc}}(x_{\text{calc}})$ and $\Delta H_{\text{calc}}(x_{\text{expt}})$, calculated from the model at those hydrogen levels, and the experimental value ΔH_{expt}. A ~0 entry for x_{expt} in Table 1 signifies that element A only dissolves a small amount of hydrogen. Values of $\Delta H_{\text{calc}}(x_{\text{expt}})$ and ΔH_{expt} have not been included in these cases since Miedema developed another expression for the heat of solution; the $x_{\text{calc}} = 0$ entry for some of these elements indicates that the model does not predict the existence of a concentrated hydride. For those elements known to form two distinct binary hydrides (the rare earths (except Eu), Nb, Pu, Th, V, Y) entries for both are given in Table 1. In view of the fact that x_{calc} is properly identified with the most stable hydride, Fig. 1 compares the single x_{calc} value with x_{expt} for the hydride of higher hydrogen content since it is more stable (i.e. its free energy and enthalpy per AH_x formula unit can be expected to be more negative).

Fig. 1 displays x_{expt} versus x_{calc} for TM binary hydrides; those considered by Bouten and Miedema [2] are denoted by the filled circles. It is clear that the qualitative agreement is very good. The largest discrepancies $\delta \equiv |x_{\text{expt}} - x_{\text{calc}}|$ occur for Ta, Ba ($\delta = 1.39$), Ag ($\delta = 1.37$), Sr ($\delta = 1.20$), and Ni ($\delta = 1.00$), with the model overestimating the observed hydrogen content in each case except Ni. The average absolute discrepancy $\bar{\delta}$, however, is only 0.38. Table 1 also shows that there is good general accord between ΔH_{expt} and either $\Delta H_{\text{calc}}(x_{\text{calc}})$ or $\Delta H_{\text{calc}}(x_{\text{expt}})$ for these TM hydrides.

Predictions extracted from the model for non-TM hydrides are included here for completeness. Fig. 2 shows that the agreement between x_{calc} and x_{expt} is poorer than for the TM hydrides in Fig. 1. The largest departures δ occur for Be ($\delta = 2.00$), Al ($\delta = 1.77$), B ($\delta = 1.40$), Cs ($\delta = 1.11$), and Rb ($\delta = 1.09$), and the mean absolute discrepancy is $\bar{\delta} = 0.78$. Similarly, comparison between the calculated and experimental enthalpies for these materials in Table 1 is less favorable than for the TM hydrides. These results substantiate Miedema's caution in restricting application of the model to TM systems. Nevertheless, Figs. 1 and 2 demonstrate that the model is capable of providing at least a qualitative indication of hydrogen capacity for most binary hydrides, including many well outside the originally intended domain of applicability of the model.

3. Ternary hydrides

Bouten and Miedema proposed [2] that the enthalpy of formation $\Delta H(AB_nH_{x+y})$ of the ternary hydride AB_nH_{x+y} relative to the parent binary AB_n and H_2 gas can be expressed in terms of binary enthalpies of formation:

$$\Delta H(AB_nH_{x+y}) = \Delta H(AH_x) + \Delta H(B_nH_y) - (1 - F)\, \Delta H(AB_n) \qquad (6)$$

Here $(x + y)$ is the known hydrogen content, and element A is assumed to form a hydride that is at least as stable as the hydride of element B. Only the values $n = 1, 2, 3, 5$ were considered, and for each n two sets of parameters (x, y, F) were given, one for smaller A atoms (Ti, Hf, Zr, V, Nb, Ta, Sc) and the other for larger A atoms (Y, rare earths, Th, U, Pu).

To predict the hydrogen content requires extension of Eq. (6) to arbitrary hydrogen level. The following *ansatz* for $\Delta H(AB_nH_x)$ enables such extension and also affords generalization to arbitrary B:A ratio n:

$$\Delta H(AB_nH_x) = \Delta H(AH_{\alpha(n)x}) + \Delta H(B_nH_{[1-\alpha(n)]x})$$
$$- \left[\frac{x}{\beta(n) + x}\right] \Delta H(AB_n) \qquad (7)$$

Table 1
Hydrogen content and enthalpies of formation for solid AH_x hydrides

Element A	x_{calc}	x_{expt}	$\Delta H_{calc}(x_{calc})$	$\Delta H_{calc}(x_{expt})$	ΔH_{expt}
Ag	1.37	~0	−31	–	–
Al	1.23	3	−25	+32	−8
Au	0.93	~0	−1	–	–
B	0	1.4	+30	+103	−8
Ba	3.39	2	−133	−176	−172
Be	0	2	0	+67	~0
Ca	2.85	2	−143	−181	−188
Cd	1.14	2[a]	−10	+7	–
Ce	3.08 (3+)	3	−142	−146	−241[b]
		2		−188	−206[b]
Co	0	0.51[c]	0	+16	+30
Cr	0.94	1	−14	−13	−12
Cs	2.11	1	−3	−2	−112
Cu	1.15	1[a]	−37	−41	–
Dy	2.88	3	−146	−140	–
		2		−188	−220
Er	2.84	3	−147	−139	–
		2		−189	−224
Eu	2.97 (2+)	2	−136	−175	–
Fe	0	~0[a]	0	–	–
Gd	2.95	3	−147	−142	–
		2		−188	−196
Ge	0	~0	0	–	–
Hf	2.48	2	−131	−156	−132
Ho	2.85	3	−144	−137	–
		2		−185	−226
Ir	0	~0	0	–	–
K	1.99	1	−15	−15	−116
La	3.15	3	−140	−147	−247[b]
		2		−187	−194
Li	1.48	1	−90	−112	−180
Lu	2.79	3	−150	−139	–
		2		−191	−208
Mg	1.73	2	−65	−54	−74
Mn	1.23	0.82[d]	−41	−50	−16
Mo	0.97	0.97[e]	−7	−7	+10
Na	1.67	1	−35	−42	−112
Nb	1.89	2	−80	−75	−60[f]
		0.5		−107	−84[f]
Nd	3.00	3	−143	−143	−244[b]
		2		−188	−211[b]
Ni	0	1[g]	0	+21	−9[g]
Os	0	0	0	0	–
Pb	0	~0	0	–	–
Pd	0	0.6	0	+10	−40
Pr	3.02	3	−143	−144	−244[b]
		2		−188	−209[b]
Pt	0	~0	0	–	–
Pu	2.16	3	−103	−63	–
		2		−110	−172
Rb	2.09	1	−10	−9	−108
Re	0	0	0	0	–
Rh	0	0.5	0	+25	+20
Ru	0	~0	0	–	–
Sc	2.53	2	−153	−187	−200
Si	0.02	~0	+3021	–	–
Sm	2.96	3	−145	−143	–
		2		−189	−200
Sn	0.08	~0	−3	–	–
Sr	3.20	2	−134	−176	−176
Ta	1.89	0.5	−80	−108	−76

Table 1. Continued

Element A	x_{calc}	x_{expt}	$\Delta H_{calc}(x_{calc})$	$\Delta H_{calc}(x_{expt})$	ΔH_{expt}
Tb	2.91	3	−146	−142	–
		2		−189	−212
Tc	0	0[a]	0	0	–
Th	3.19	15/4[a]	−145	−120	–
		2		−196	−146
Ti	2.03	2	−110	−111	−136
Tm	2.80	3	−147	−137	–
		2		−188	−224
U	2.26	3	−97	−65	−84
V	1.46	2	−58	−35	−40[h]
		0.5		−75	−70
W	0	~0	0	–	–
Y	2.95	3	−145	−142	–
		2		−188	−228
Yb	2.77 (2+)	2.55[b]	−142	−153	–
		2		−178	−182
Zn	1.10	2[c]	−23	+7	–
Zr	2.62	2	−148	−182	−164

x_{calc} is the value of x which minimizes $\Delta H(AH_x)$ in Miedema's model; x_{expt} is the observed hydrogen content; $\Delta H_{calc}(x_{calc})$ and $\Delta H_{calc}(x_{expt})$ are the enthalpies of formation calculated from the model at those two hydrogen levels, and ΔH_{expt} is the experimental enthalpy of formation (all in kJ/mol H$_2$). Unless noted otherwise, the x_{expt} and ΔH_{expt} entries are from Ref. [6].

[a] Ref. [7].
[b] Ref. [8].
[c] Ref. [9].
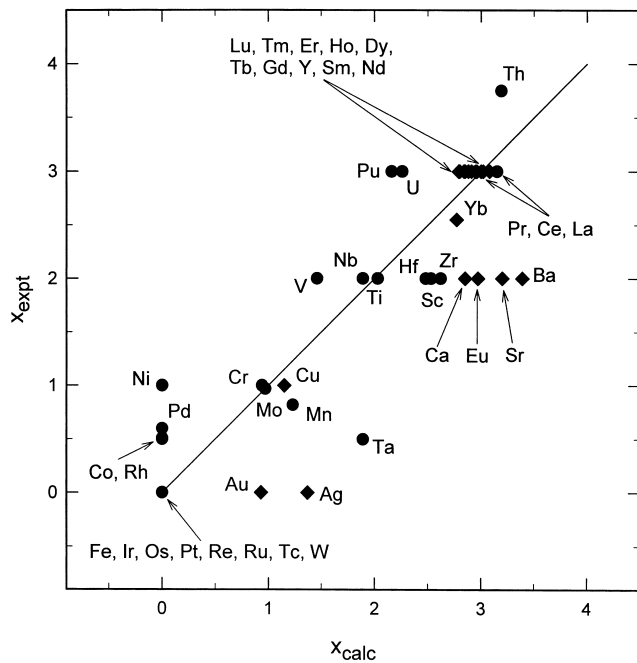[d] Ref. [10].
[e] Ref. [11].
[f] Ref. [2].
[g] Ref. [12].
[h] Ref. [13].

Fig. 1. Comparison of experimental hydrogen content x_{expt} and that predicted by Miedema's model, x_{calc}, for binary transition metal (TM) hydrides AH$_x$. Filled circles represent the hydrides considered by Bouten and Miedema [2]; diamonds correspond to other TM hydrides. The solid line is the locus of points for which $x_{expt} = x_{calc}$.
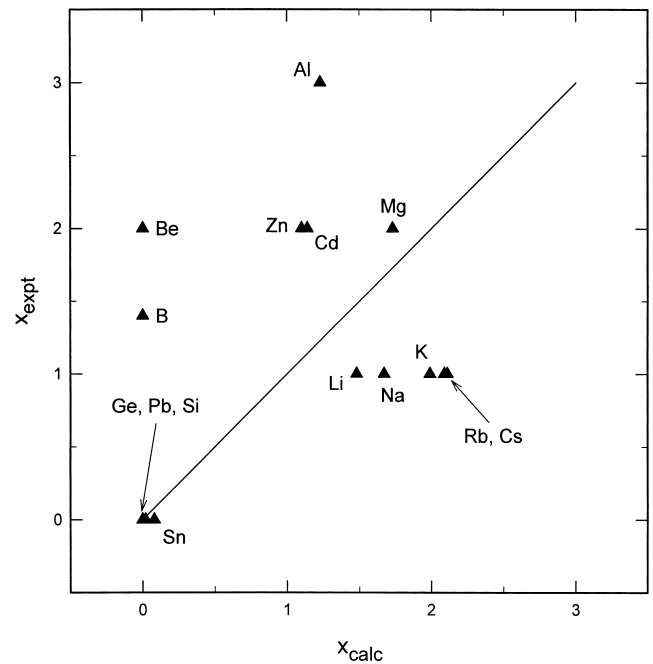

Fig. 2. Comparison of x_{expt} and x_{calc} for non-TM binary hydrides AH$_x$.

The choice of the prefactor $\eta(x,n) \equiv [x/\beta(n) + x]$ is motivated by insistence on two reasonable limits:

(1) $\lim_{x \to 0} \eta(x, n) = 0$. For both A and B metals this ensures

that $\lim_{x \to 0} \Delta H(AB_n H_x) = 0$; the enthalpy of formation of the ternary hydride must tend to zero with hydrogen content since the reference material is the AB_n binary.[1]

(2) $\lim_{x \to \infty} \eta(x, n) = 1$. This preserves the central concept underlying Eq. (6) that hydriding AB_n leads to the local formation of the hydride AH_x via breaking of A–B bonds, the energy penalty for which is approximated by the $(1-F)$ term; clearly the maximum number of A–B bonds broken upon formation of the ternary hydride corresponds to the subtraction of at most $\Delta H(AB_n)$ on the right side of Eq. (7).

Eq. (7) should also maintain the proper binary hydride limits

(3) $\lim_{n \to 0} \Delta H(AB_n H_x) = \Delta H(AH_x)$;
(4) $\lim_{n \to \infty} \Delta H(AB_n H_x) = \Delta H(B_n H_x)$.

To preserve correspondence with Eq. (6) it must also be demanded that

(5) $\eta(x + y) = (1 - F)$ for $n = 1, 2, 3, 5$.

With $\Delta H(AB_n H_x)$ in the form of Eq. (7) conditions (1) and (2) are met automatically. Conditions (3) and (4) lead to corollary limits on $\alpha(n)$ and $\beta(n)$:

$$\lim_{n \to 0} \alpha(n) = 1 \tag{8a}$$

$$\lim_{n \to \infty} \alpha(n) = 0 \tag{8b}$$

$$\lim_{n \to 0} \beta(n) = \infty \tag{8c}$$

$$\lim_{n \to \infty} \beta(n)/n = \infty. \tag{8d}$$

All five conditions are satisfied by the following simple polynomial expressions:

smaller A atoms

$$\alpha(n) = \begin{cases} 1 - \dfrac{277}{560}n^2 + \dfrac{137}{560}n^3 & n \leq 1 \\[2mm] \dfrac{1}{1120}(-13n^3 + 138n^2 - 523n + 1238) & 1 \leq n \leq 5 \\[2mm] \dfrac{1}{112n}\left(153 + \dfrac{355}{n}\right) & n \geq 5 \end{cases}$$
$$\tag{9a}$$

$$\beta(n) = \begin{cases} \dfrac{3}{2}\left(n + \dfrac{1}{n}\right) & n \leq 1 \\[2mm] \dfrac{1}{27}(-17n^3 + 50n^2 - 49n + 97) & 1 \leq n \leq 2 \\[2mm] \dfrac{1}{81}(-7n^3 + 100n^2 - 475n + 795) & 2 \leq n \leq 5 \\[2mm] \dfrac{1}{9}(n^2 - 10n + 30) & n \geq 5 \end{cases}$$
$$\tag{9b}$$

larger A atoms

$$\alpha(n) = \begin{cases} 1 - \dfrac{289}{720}n^2 + \dfrac{29}{144}n^3 & n \leq 1 \\[2mm] \dfrac{1}{1440}(n^3 + 30n^2 - 349n + 1470) & 1 \leq n \leq 5 \\[2mm] \dfrac{1}{144n}\left(665 - \dfrac{1825}{n}\right) & n \geq 5 \end{cases}$$
$$\tag{10a}$$

$$\beta(n) = \begin{cases} \dfrac{15}{8}\left(n + \dfrac{1}{n}\right) & n \leq 1 \\[2mm] \dfrac{1}{48}(7n^3 - 80n^2 + 139n + 114) & 1 \leq n \leq 2 \\[2mm] \dfrac{1}{144}(-11n^3 + 164n^2 - 815n + 1446) & 2 \leq n \leq 5 \\[2mm] \dfrac{1}{48}(7n^2 - 70n + 207) & n \geq 5 \end{cases}$$
$$\tag{10b}$$

Plots of $\alpha(n)$ and $\beta(n)$ are displayed in Fig. 3. The form of Eq. (7) and the choices of $\alpha(n)$ and $\beta(n)$ in Eqs. (9) and

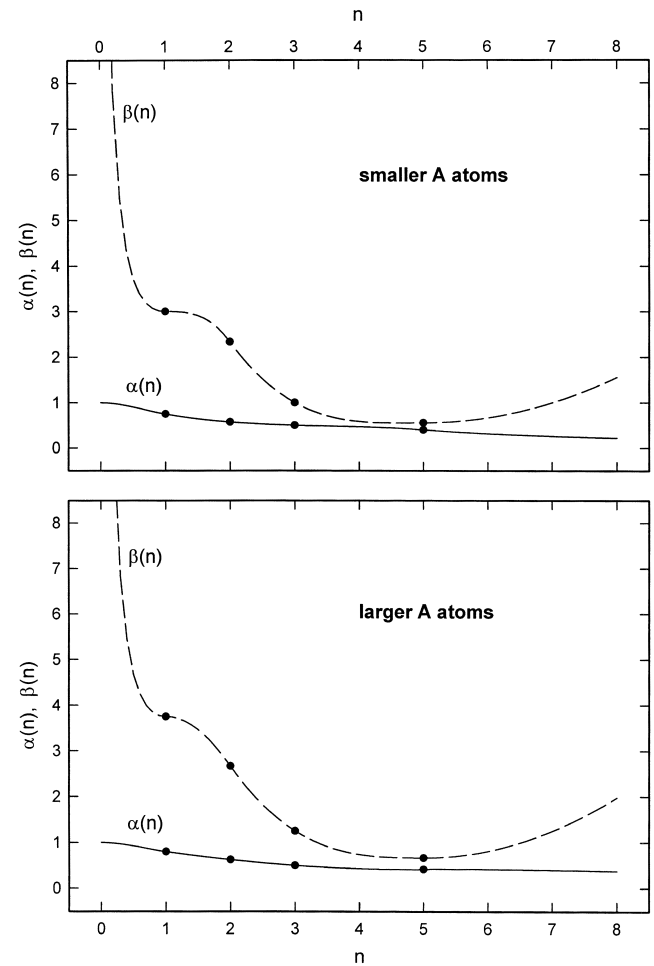Fig. 3. Upper panel: $\alpha(n)$ and $\beta(n)$ for smaller A atoms (Eq. (9)). Lower panel: $\alpha(n)$ and $\beta(n)$ for larger A atoms (Eq. (10)). Solid dots correspond to values reproducing Miedema's model, Eq. (6), for $n = 1, 2, 3, 5$.

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[1] In general the correct limit is $\lim_{x \to 0} \Delta H(AB_n H_x) = \Delta H_{trans}(A) + n \Delta H_{trans}(B)$, which is non-zero only if A or B is non-metallic.

(10) are not unique. Nonetheless, by satisfying the five conditions above, in particular the demand that Eq. (7) reduce to Eq. (6) for $n = 1, 2, 3, 5$ (condition (5)), they ensure firm contact with Miedema's original model and provide reasonable extension to arbitrary x and n.

As for the binary hydrides, the hydrogen content x characterizing the most stable ternary hydride AB_nH_x can be extracted from the model by using Eq. (7) to determine the value of x which minimizes $\Delta H(AB_nH_x)$. This minimum enthalpy of formation can also be identified (with opposite sign) as the heat of reaction for

$$AB_n + \frac{1}{2}xH_2 \rightarrow AB_nH_x \tag{11}$$

or, equivalently, as the heat of formation of AB_nH_x from AB_n and H_2 gas.

Tables 2 and 3 and Figs. 4 and 5 present results for 89 known ternary hydride systems. In the 53 entries of Table 2 and Fig. 4 both A and B are transition metal elements; those systems conform to Miedema's original compositional restrictions (ignoring the fact that some of the A:B ratios n are other than 1, 2, 3, 5 to which the model was also confined). All compositions in Table 3 and Fig. 5, on the other hand, contain at most one TM and are outside Miedema's domain of application.

Figs. 4 and 5 display x_{expt}/M versus x_{calc}/M, where M is the number of A and B atoms in a formula unit. In addition to x_{calc}, x_{expt}, $\Delta H_{calc}(x_{calc})$, $\Delta H_{calc}(x_{expt})$, and ΔH_{expt}, Tables 2 and 3 also list the calculated enthalpy of formation $\Delta H(AB_n)$ of the parent binary. It should be emphasized that there can be some uncertainty as well as variation in x_{expt} and ΔH_{expt} for a given material. In some cases, presumably those in which there is more than one hydride phase, x_{expt} represents the hydrogen content at the maximum pressure applied, but in others it denotes the width of the first plateau in an isothermal pressure–composition measurement. The distinction is not always clear. Only the tabulations in Ref. [14] consistently provide both values where available. The second is given in parentheses next to the first in Tables 2 and 3, and the first is compared with x_{calc} in Figs. 4 and 5; the model yields only one hydride content for a given parent binary composition, and in these cases it is appropriately compared with the larger observed content.

There is broad semi-quantitative agreement between x_{expt}/M and x_{calc}/M in Fig. 4, although in general the calculated results exceed the experimental values. For many of these TM-only hydrides Table 2 indicates reasonable quantitative correspondence between ΔH_{expt} and either $\Delta H_{calc}(x_{calc})$ or $\Delta H_{calc}(x_{expt})$. The largest discrepancies $\delta \equiv |x_{expt} - x_{calc}|/M$ in hydrogen content per atom occur for $LaIr_2H_x$ ($\delta = 1.36$), $HfFe_2H_x$ ($\delta = 1.28$), $HfPtH_x$ ($\delta = 1.21$), and $TiFe_2H_x$ ($\delta = 1.05$), four of the six materials listed in Table 2 which are not known to form hydrides ($x_{expt} = 0$). These deviations may underscore one major shortcoming of the model, namely, its neglect of structure-

dependent enthalpy contributions. $LaIr_2$ is characterized by the cubic Laves phase $MgCu_2$ structure, $HfFe_2$ and $TiFe_2$ crystallize in the hexagonal Laves phase $MgZn_2$ structure, and $HfPt$ has the cubic CsCl structure. The departures suggest that structural enthalpy terms may be significant not only for hydrides of Laves phases, as Buschow et al. [18] have speculated via comparison of experimental and calculated formation enthalpies, but for hydrides of other high-symmetry structures as well.

Surprisingly, the overall correspondence between x_{expt}/M and x_{calc}/M in Fig. 5 for materials outside Miedema's composition range is of the same level as that in Fig. 4. This provides some encouragement and justification for extending the model both to non-TM components and to other B:A ratios. The largest deviations δ are associated with MgB_2H_x ($\delta = 1.76$), $MgAl_2H_x$ ($\delta = 1.54$), $CaMg_2H_x$ ($\delta = 1.31$), $LiBH_x$ ($\delta = 1.05$), and $LiAlH_x$ ($\delta = 0.98$). Excepting $CaMg_2H_x$ (for which $x_{expt} = 1.3$ appears to be low), these materials are complex hydrides in the sense that they contain ionic hydride complexes such as $(AlH_4)^-$ and $(BH_4)^-$ and are more informatively written as $Mg(BH_4)_2$, $Mg(AlH_4)_2$, etc. Even though such materials fall well outside Miedema's original domain, there is reasonable correspondence between the experimental and predicted hydrogen content for other complex hydrides, such as $Mg_2(Fe, Co, Ni, Cu)H_x$ containing one TM component, in Table 3 and Fig. 5.

The calculated formation enthalpy $\Delta H(AB_n)$ is positive for 10 of the parent binary compositions in Table 3. This is correct for LiB, NaB, Na_3Al, NaAl, Mg_2Fe, Mg_2Co, Mg_2Os, and Cs_3Cd, inasmuch as these compounds are not known to form. The prediction is incorrect by only a small margin for the extant compound Mg_2Si [$\Delta H(Mg_2Si) = +2$ kJ/f.u.] but fails badly for the known boride MgB_2 [$\Delta H(MgB_2) = +44$ kJ/f.u.].

Since $\Delta H(AB_nH_x)$ represents the enthalpy of formation of AB_nH_x hydride relative to its parent binary AB_n and H_2 gas, its meaning is unclear if AB_n does not form. In such cases an unambiguous alternative measure of stability is provided by the calculated formation enthalpy ΔH^* of AB_nH_x from its elemental constituents. This quantity, in units of kJ/f.u., can be obtained from the second, fourth, and sixth columns of Table 2:

$$\Delta H^* \equiv \frac{1}{2}x_{calc} \cdot [\Delta H_{calc}(x_{calc}) \,(kJ/mol\, H_2)]$$
$$+ \Delta H(AB_n) \,(kJ/f.u.) \tag{12}$$

It is listed in the final column of the table for the 10 materials having $\Delta H(AB_n) > 0$. ΔH^* is properly negative for all except $NaBH_x$ and MgB_2H_x. The failure of the model in the latter two cases emphasizes the potentially large uncertainties accompanying its application to materials having no TM component in addition to forming complex hydrides such as $Na(BH_4)$ and $Mg(BH_4)_2$.

Fewer ΔH_{expt} values are available for the hydrides in

Table 2

Hydrogen content and enthalpy of formation for ternary AB_nH_x hydrides from the extended Miedema model; both A and B are transition metals

Hydride	x_{calc}	x_{expt}	$\Delta H_{calc}(x_{calc})$	$\Delta H_{calc}(x_{expt})$	ΔH_{expt}	$\Delta H(AB_n)$
$CaNi_3H_x$	5.16	4.5[a]	−56	−62	−58[a]	−40
$CaNi_5H_x$	6.18	4.5[a]	−42	−50	−38[a]	−42
$ScFe_2H_x$	4.07	3.2 (2.0)[b]	−74	−89 (−99)	−30[a]	−47
$TiCr_2H_x$	3.57	1.2[b]	−59	−78	−23[b]	−30
$TiFeH_x$	2.52	1.6[a]	−67	−86	−34[a]	−50
$TiFe_2H_x$	3.16	0[a]	−40	0	–	−66
$TiCoH_x$	2.41	1.5[a]	−56	−71	−62[a]	−85
$TiCuH_x$	2.79	1.0[a]	−82	−114	−76[a]	−27
$Y_6Fe_{23}H_x$	36.60	21.5[a]	−60	−78	<−72[a]	−34
YCo_3H_x	5.20	4.0 (1.0)[b]	−40	−47 (−3)	−56[b]	−103
YNi_3H_x	5.07	4.0[a]	−26	−28	−46[a]	−148
ZrV_2H_x	5.10	5.3[a]	−101	−97	−200[b]	−15
$ZrCr_2H_x$	4.42	3.8[b]	−78	−89	−46[b]	−50
$ZrMn_2H_x$	4.70	3.6[a]	−84	−103	−44[a]	−64
$ZrNiH_x$	3.04	2.8[a]	−73	−78	−66[a]	−143
$ZrPd_2H_x$	0	0[a]	0	0	–	−354
$LaCo_5H_x$	6.72	9.0 (3.4)[b]	−31	−18 (−30)	−45[b]	−89
$LaNiH_x$	3.70	4.0[a]	−95	−87	−126[a]	−75
$LaNi_2H_x$	4.46	4.6 (2.0)[b]	−58	−56 (−68)	−55[b]	−117
$LaNi_5H_x$	6.57	6.7 (5.5)[b]	−16	−16 (−17)	−30[b]	−141
$LaCu_5H_x$	8.24	3.72[c]	−53	−59	−43[c]	−110
$LaRh_2H_x$	4.21	4.9 (1.4)[b]	−32	−26 (−14)	−44[b]	−209
$LaIr_2H_x$	4.07	0[a]	−30	0	–	−198
$LaPt_5H_x$	0	1.2[a]	0	314	−26[a]	−357
$CeCo_2H_x$	4.49	4.1[a]	−68	−74	<−72[a]	−80
$CeCo_3H_x$	5.43	3.8[a]	−43	−51	−46[a]	−91
$Ce_2Co_7H_x$	11.74	9.0 (6.1)[b]	−36	−42 (−36)	−44[b]	−186
$CeCo_5H_x$	6.58	3.0[a]	−30	−22	−38[a]	−96
$CeNi_2H_x$	4.36	3.9[a]	−57	−62	<−72[a]	−122
$CeNi_3H_x$	5.30	4.2[a]	−29	−32	−44[a]	−138
$Ce_2Ni_7H_x$	11.48	4.2[a]	−21	+12	−46[a]	−284
$CeNi_5H_x$	6.44	6.0[a]	−14	−15	−14[a]	−146
$NdCu_5H_x$	7.97	3.0[b]	−53	−51	–	−111
$EuNi_5H_x$	6.42	5.5 (1.2)[a]	−46	−51 (−45)	−26[a]	−19
$GdMn_2H_x$	5.01	3.0[b]	−101	−138	−88[b]	−6
$GdFe_3H_x$	5.44	3.2[b]	−69	−92	−51[b]	−5
$GdCo_2H_x$	4.27	4.5[a]	−66	−63	−54[a]	−92
$GdCo_3H_x$	5.20	5.0 (2.0)[b]	−40	−42 (−32)	−52[b]	−103
$Gd_2Co_7H_x$	11.27	9.0 (2.6)[b]	−33	−37 (+10)	−58[b]	−211
$GdCo_5H_x$	6.32	2.2[a]	−26	−1	−30[a]	−108
$GdNi_2H_x$	4.14	4.1[b]	−55	−56	−90[b]	−133
$GdNi_5H_x$	6.18	2.9[a]	−11	+12	−26[a]	−156
$GdRu_2H_x$	3.96	3.7 (2.7)[b]	−48	−51 (−57)	−60[b]	−137
$GdRh_2H_x$	3.87	3.3 (2.8)[b]	−30	−33 (−33)	−49[b]	−221
$DyRu_2H_x$	3.84	3.1[a]	−47	−54	−56[a]	−143
$ErFe_2H_x$	4.32	4.2 (2.0)[b]	−86	−88 (−119)	−58[b]	−19
$ErFe_3H_x$	5.23	4.0[b]	−66	−80	−44[b]	−22
$YbNiH_x$	3.36	2.7[a]	−106	−126	−146[a]	−24
$YbNi_2H_x$	4.15	3.1[a]	−77	−93	−52[a]	−36
$YbNi_5H_x$	6.01	3.0[a]	−41	−48	−26[a]	−41
$HfFe_2H_x$	3.84	0[a]	−50	0	–	−85
$HfPtH_x$	2.42	0[a]	−18	0	–	−268
UPd_3H_x	0	0[a]	0	0	–	−243

x_{calc} is the value of x which minimizes $\Delta H(AB_nH_x)$ specified by Eq. (7); x_{expt} is the observed hydrogen content; $\Delta H_{calc}(x_{calc})$ and $\Delta H_{calc}(x_{expt})$ are the enthalpies of formation calculated from the model at those two hydrogen levels, and ΔH_{expt} is the experimental enthalpy of formation (all in kJ/mol H_2). $\Delta H(AB_n)$ is the calculated enthalpy of formation of the parent binary in kJ/f.u.

[a] Ref. [6].

[b] Ref. [14].

[c] Ref. [15].

Table 3
Hydrogen content and enthalpy of formation for ternary AB_nH_x hydrides from the extended Miedema model Eq. (7); at most one of the elements A, B is a transition metal

Hydride	x_{calc}	x_{expt}	$\Delta H_{calc}(x_{calc})$	$\Delta H_{calc}(x_{expt})$	ΔH_{expt}	$\Delta H(AB_n)$	ΔH^*
$LiBH_x$	1.91	4	−33	+27	–	+14	−17
Li_3AlH_x	4.67	6	−86	−59	–	−15	
$LiAlH_x$	2.03	4	−69	−1	–	−11	
$LiPdH_x$	1.66	0.8[a]	−27	−26	−76[a]	−110	
$LiPtH_x$	1.68	0.7[a]	−32	−32	−134[a]	−88	
$NaBH_x$	2.22	4	−17	+16	–	+80	+61
Na_3AlH_x	5.33	6	−38	−33	–	+44	−57
$NaAlH_x$	2.32	4	−44	−4	–	+39	−11
MgB_2H_x	2.72	8[b]	+5	+60	–	+44	+51
$Mg_{17}Al_{12}H_x$	29.64	24.9[b]	−65	−74	–	−14	
$Mg_2Al_3H_x$	5.83	4.4[b]	−47	−56	−63[b]	−13	
$MgAl_2H_x$	3.37	8[b]	−43	+20	–	−7	
Mg_2SiH_x	3.81	1.6[b]	−41	−33	–	+2	−76
Mg_2FeH_x	3.92	6[b]	−65	−27	−79[b]	+52	−76
Mg_2CoH_x	3.79	5[c]	−58	−38	−86[c]	+2	−108
Mg_2NiH_x	3.73	4[a]	−55	−51	−64[a]	−19	
Mg_2CuH_x	3.87	3.0[b]	−59	−71	−73[b]	−17	
$Mg_7Zn_3H_x$	13.10	11.4[b]	−60	−67	–	−38	
Mg_2OsH_x	3.75	6[b]	−57	−18	–	+11	−97
Mg_2PbH_x	3.68	2.8[b]	−53	−63	–	−33	
$CaMg_2H_x$	5.22	1.3[b]	−100	−139	–	−30	
$TiBe_2H_x$	2.68	3.0[a]	−12	−10	−38 to −26[a]	−135	
$ZrBe_2H_x$	3.51	1.5[a]	−25	−12	<−54[a]	−194	
$ZrBe_5H_x$	0	0.2[a]	0	+530	−48[a]	−229	
Cs_3CdH_x	6.64	5[d]	−4	−4	–	+3	−10
$LaMg_2H_x$	5.76	7.0[b]	−98	−77	–	−36	
$La_2Mg_{17}H_x$	28.26	33[e]	−69	−57	–	−78	
$LaMg_{12}H_x$	19.98	20[e]	−64	−64	–	−39	
$CeMg_2H_x$	5.65	7.0[b]	−98	−75	–	−34	
$Ce_5Mg_{41}H_x$	67.50	86[e]	−69	−51	–	−186	
$Ce_2Mg_{17}H_x$	27.89	31[e]	−69	−61	–	−74	
$CeMg_{12}H_x$	19.82	20 (2)[e]	−64	−63	–	−37	
$NdMg_2H_x$	5.53	4.0[e]	−99	−126	–	−33	
$SmMg_2H_x$	5.46	3.0[e]	−100	−141	–	−31	
$HfAlH_x$	3.03	1.0[a]	−64	−75	–	−150	
Th_2AlH_x	6.67	4.0[a]	−122	−165	–	−158	

ΔH^* is given in kJ/f.u. by Eq. (12); other quantities as in Table 2.
[a] Ref. [6].
[b] Ref. [15].
[c] Ref. [16].
[d] Ref. [17].
[e] Ref. [14].

Table 3. Where comparison can be made, ΔH_{expt} is more negative than either $\Delta H_{calc}(x_{calc})$ or $\Delta H_{calc}(x_{expt})$.

4. Remarks

It has been shown that Miedema's model is capable of predicting the hydrogen content of binary and ternary hydrides in addition to providing an estimate of the enthalpy of formation ΔH. For ternary AB_nH_x hydrides the model has been extended by means of a reasonable *ansatz* to arbitrary hydrogen content x and arbitrary B:A ratio n.

Results for the ternary systems suggest that the extended model may have applicability beyond Miedema's original restriction to TM parent elements. For Mg-containing materials in particular the model correctly predicts the existence of hydrides such as Mg_2FeH_x and Mg_2OsH_x for which the parent compounds are correctly predicted not to form. This opens the possibility that the model can serve as a useful qualitative guide to the discovery of new Mg-based hydrides.

Phenomenological models remain of interest for hydride research in view of the fact that ΔH is a challenge to obtain via ab initio electronic structure calculations. Two such calculations for ternary metallic hydrides have been reported recently. Nakamura et al. [19] find $\Delta H(LaNi_5H_7) = -57$ kJ/mol H_2, while $\Delta H_{calc}(x_{calc}) = -16$ kJ/mol H_2 for $LaNi_5H_{6.57}$ from the Miedema model and $\Delta H_{expt} = -30$ kJ/mol H_2 in Table 2. García et al. [20] obtain $\Delta H(Mg_2NiH_4) = -7$ kJ/mol H_2, to be compared

model agrees better with experiment in each case. Given the difficulty of deriving ΔH from first principles even when the compositions and crystal structures are known, ab initio prediction of new hydrides will continue to be a vastly greater challenge.

Acknowledgements

Fig. 4. x_{expt}/M versus x_{calc}/M for ternary $A_{n_A}B_{n_B}H_x$ hydrides with both A and B transition metals. x_{expt} is the experimental hydrogen content, and x_{calc} is calculated via Eq. (7); $M \equiv n_A + n_B$.

with $\Delta H_{calc}(x_{calc}) = -55$ kJ/mol H$_2$ for Mg$_2$NiH$_{3.73}$ and $\Delta H_{expt} = -64$ kJ/mol H$_2$ in Table 3. ΔH from Miedema's

Fig. 5. x_{expt}/M versus x_{calc}/M for ternary $A_{n_A}B_{n_B}H_x$ hydrides with at most one TM element; $M \equiv n_A + n_B$.

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