Predicting formation enthalpies of metal hydrides

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Anders Andreasen
Abstract:

In order for the hydrogen based society viz. a society in which hydrogen is the primary energy carrier to become realizable an efficient way of storing hydrogen is required. For this purpose metal hydrides are serious candidates. Metal hydrides are formed by chemical reaction between hydrogen and metal and for the stable hydrides this is associated with release of heat ($\Delta H_f$). The more thermodynamically stable the hydride, the larger $\Delta H_f$ and the higher temperature is needed in order to desorpb hydrogen (reverse reaction) and vice versa. For practical application the temperature needed for desorption should not be too high i.e. $\Delta H_f$ should not be too large. If hydrogen desorption is to be possible below 100°C (which is the ultimate goal if hydrogen storage in metal hydrides should be used in conjunction with a PEM fuel cell), $\Delta H_f$ should not exceed -48 kJ/mol. Until recently only intermetallic metal hydrides with a storage capacity less than 2 wt.% H$_2$ have met this criterion. However, discovering reversible hydrogen storage in complex metal hydrides such as NaAlH$_4$ (5.5 wt. % reversible hydrogen capacity) have revealed a new group of potential candidates. However, still many combination of elements from the periodic table are yet to be explored. Since experimental determination of thermodynamic properties of the vast combinations of elements is tedious it may be advantageous to have a predictive tool for this task. In this report different ways of predicting $\Delta H_f$ for binary and ternary metal hydrides are reviewed. Main focus will be on how well these methods perform numerically i.e. how well experimental results are resembled by the model. The theoretical background of the different methods is only briefly reviewed.
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1 Introduction

1.1 Towards the hydrogen based society

A growing interest in the transformation of the hydrocarbon based society into a hydrogen based society is emerging around the world. This is induced by the fact that hydrogen offers some key advantages compared to hydrocarbons: Produced by electrolysis of water using renewable energy sources e.g. solar, wind or water power as a source of electricity the need for hydrocarbons is greatly reduced. Further, converting the chemically stored energy in H\textsubscript{2} to electricity in a fuel cell under the right conditions water is the only combustion product.

However, for the hydrocarbon based society to become realizable a suitable way of storing hydrogen in between the production and the use of hydrogen must be offered. This is indeed a problem that needs special attention if hydrogen should become the future choice of energy carrier in mobile applications e.g. cars due to the very specific demands for safety, volumetric energy density, gravimetric energy density etc. [1]. Different ways of storing hydrogen exist e.g storage in high pressure cylinders, storage as liquid hydrogen, physisorption in carbon nanotubes and storage in metal hydrides [2]. In our view the storage of hydrogen in metal hydrides is perhaps the most interesting and challenging [3].

1.2 Hydrogen storage in metals

Storage of hydrogen in metal hydrides is possible since many metals react readily with hydrogen forming a stable metal hydride. For instance, Mg reacts with hydrogen forming a hydride of the form MgH\textsubscript{2}. Thus, storing 7.6 wt. % of hydrogen and thereby fulfilling the gravimetric hydrogen density criterion suggested by the U.S. Department of Energy for year 2010 [4]. However, in order to release hydrogen at a pressure of 1 bar the hydride must be heated to above 280°C. This is because magnesium forms a (too) stable hydride with a heat of formation of approx. ΔH\textsubscript{f}=-75 kJ/mol. A car driven by a PEM fuel cell operated at around 80-100°C is not capable of supplying the required heat for this operation (in fact 100°C is the upper operable temperature limit for metal hydrides suggested by USDOE [4]). Alternatively, the hydride bed may be heated by combustion of hydrogen. This will however lower the efficiency by approx. 25 % [2]. Another way around this problem is to use another hydride material with improved thermodynamical properties e.g. LaNi\textsubscript{5} or FeTi which deliver hydrogen at temperatures as low as 12°C and -8°C, respectively. These materials do however fail to meet the gravimetric energy density criterion since they store only 1.5 wt. % and 1.85 wt. % of hydrogen, respectively [5]. To the best of our knowledge no material have been found with properties fulfilling both the energy density criterion and the thermodynamic criterion. So the search continues and new combinations of metals in intermetallic compounds are proposed, prepared and tested experimentally for their hydrogen storage properties. But how do we propose new materials for synthesis with the desired thermodynamic properties? One method is trial-and-error e.g. making slight modifications of a compound with known properties. However, this is indeed a tedious and time consuming approach. Another way is by prediction of the desired properties by calculation either from empirical knowledge or from first principle.
1.3 Outline

In this report different ways of predicting hydride formation enthalpies are evaluated. A number of different approaches will be analyzed ranging from simple models such as Born-Haber cycle, the Miedema model to more advanced methods like Effective Medium Theory and Density Functional Theory. This report is neither intended as a step-by-step guide for performing these calculations nor is it intended as a detailed description of the theoretical basis of the different models. The main goal is to review the results of the different approaches. The organization of this report is the following: In section 2 we will describe the use of experimentally determined Pressure Composition Isotherms as a tool for deriving thermodynamic parameters. In section 3 a number of different ways of predicting the formation enthalpy of binary metal hydrides will be discussed ranging from empirical/semi-empirical methods to non-empirical methods. In section 4 we expand the picture to account for prediction of formation enthalpies of ternary metal hydrides. The review of methods of predicting the hydride formation enthalpy is by no means intended to give a complete overview of available methods. For instance known methods e.g. the correlation between interstitial hole size and thermodynamic properties of intermetallic compounds proposed by Lundin et al. [6] and the band structure model proposed by Greissen et al. [7] are excluded.
2 Thermodynamic properties from experiments

2.1 The Pressure Composition Isotherm

The Pressure Composition Isotherm from now on called PCI is the work horse when it comes to determination of several key properties of metal hydrides. A generic PCI is depicted in figure 1 (left). When initially increasing the hydrogen pressure at isothermal conditions the adsorbed amount of hydrogen (H/M is the hydrogen to metal stoichiometric ratio) will increase only slightly. This corresponds to the formation of a solid solution of hydrogen and this is denoted the \( \alpha \)-phase. When the maximum solubility of hydrogen in the \( \alpha \)-phase is reached the hydride phase (\( \beta \)-phase) will start forming. Increasing the hydrogen pressure further will now result in a substantial increase in the absorbed amount of hydrogen. This phenomenon may be explained from the Gibbs phase rule [8]

\[
F = 2 - \pi + N
\]

(1)

where \( F \) is the degree of freedom, \( \pi \) is the number of phases and \( N \) is the number of chemical species. Thus, the addition of one additional phase is counterbalanced by the loss of a degree of freedom. The pressure at which this transformation takes place is referred to as the plateau pressure and in this region the \( \alpha \)-phase and \( \beta \)-phase co-exist. When the stoichiometric hydride have formed completely depleting the \( \beta \)-phase one additional degree of freedom is regained and the additional absorption of hydrogen will now require a huge pressure increase. This corresponds to the solid solution of hydrogen in the \( \beta \)-phase. The plateau pressure gives us valuable information about reversible storage capacity from the width of the plateau and the position of the plateau at a given temperature may give an idea of the stability of the hydride. Stable hydrides (\( \Delta H_f << 0 \)) will require higher temperatures than less stable hydrides (\( \Delta H_f < 0 \)) to reach a certain plateau pressure. Making series of PCI’s at different temperatures it is even possible to construct a phase diagram from the end points of the plateaus in the individual PCI’s. This

![Figure 1. Left: Pressure-Composition-Isotherms (PCI) for a hypothetical metal hydride. Adapted from ref. [1]. Right: Van’t Hoff plot for a hypothetical metal hydride derived from the measured pressures at plateau midpoints from the PCI’s.](image-url)
is shown by the dashed line in figure 1.

2.2 Thermodynamic properties from PCI

At the midpoint of the plateau the following equilibrium is assumed to exist between gas phase hydrogen + pure metal and the $\beta$-phase to exist:

$$H_2(g) + Me_{pure}(s) \rightleftharpoons Me_\beta(s)$$

thus assuming the amount of hydrogen dissolved in the metal lattice to be negligible. At equilibrium the reaction quotient $Q$ equals the equilibrium constant $K$.

$$K = \prod_i (\tilde{a}_i)^{\nu_i}$$

where $\tilde{a}_i$ is the activity coefficient of species $i$ and $\nu_i$ is the stoichiometric coefficient of species $i$. Substituting from eq. 2 assuming the ideal gas description to be valid i.e. $\tilde{a}_{H_2} = p_{H_2}/p^\circ$ where $p^\circ$ is the thermodynamic reference pressure and assuming that $\tilde{a}_{Me_{pure}} = \tilde{a}_{Me_\beta} = 1$ we get

$$K^{-1} = \frac{p_{H_2}}{p^\circ}$$

From the definition of the equilibrium constant we know that $-RT \ln K = \Delta G^\circ$, where $\Delta G^\circ$ is the change in standard Gibbs free energy upon hydrogenation. Further the definition of $\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$ inserted into the equation above yields

$$\ln \left( \frac{p_{H_2}}{p^\circ} \right) = \frac{\Delta H^\circ}{RT} - \frac{\Delta S^\circ}{R}$$

where $\Delta H^\circ$ and $\Delta S^\circ$ is the change in standard enthalpy and the change in standard entropy, respectively. Rearranging eq. 5 gives

$$\Delta H_f = \Delta S_f T$$

Hence, if the entropy change upon hydrogenation is more or less the same regardless of the host metal a plot of the formation enthalpy vs. plateau temperature at 1 bar $H_2$ should lie on a straight line with slope $\Delta S_f$. According to fig. 3 this is

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Figure 2. Left: Pressure-Composition-Isotherms (PCI) for LaNi$_5$. Right: Van’t Hoff plot measured pressures at plateau midpoints (H/M=0.5) from the PCI’s. The Van’t Hoff plot of Lundin et al. is from ref. [9]. PCI measurements were performed on a high pressure balance described in detail elsewhere [10].

Figure 3. Hydride formation enthalpy, $\Delta H_f$ per mole H$_2$ as a function of the plateau temperature at 1 bar. The plateau temperature is calculated from reported thermodynamic parameters using the Van’t Hoff equation. Data represented by circles is from ref. [11], data represented by squares is taken from ref. [12] and data represented by diamonds is taken from ref. [5].

actually the case. The straight line depicted in the figure has slope $\Delta S_f = -130$ J/(mol K). The entropy loss of 130 J/(mol K) roughly corresponds to the loss of the translational degree of freedom when H$_2$ from the gas phase is absorbed in the metal$^1$.

As stated earlier the USDOE criterion regarding thermodynamics for a hydrogen storage material is desorption of hydrogen above 1 bar to be possible below 100 °C

$^1$A back-on-the-envelope calculation using statistical thermodynamics of the translational contribution to the overall entropy using $S = R \ln(Q) + RT \left( \frac{d \ln(Q)}{d T} \right)_V$, where Q is the translational partition function gives 116 J/(mol K).
Eq. 6 can now be applied to reformulate this criterion in terms of $\Delta H_f$. We find that in order for a metal hydride to meet the USDOE criterion $\Delta H_f$ should not be more exothermic than 48 kJ/mol.
3 Binary hydrides

3.1 Born-Haber calculations

The Born-Haber cycle is often applied as a textbook example of evaluating the formation enthalpies of ionic crystals. The formation of a binary hydride can be described by the following overall reaction

\[ \text{Me}(s) + \frac{n}{2} \text{H}_2(g) \rightarrow \text{MeH}_n(s) \] (7)

The heat of formation of the metal hydride, \( H_f \), can be determined from calorimetric experiments or derived from PCI-measurements. However, if these experiments are unavailable we may derive it by constructing a Born-Haber thermodynamic cycle as shown in figure 4.

\[ \text{Me}(s) + \frac{n}{2} \text{H}_2(g) \rightarrow \text{MeH}_n(s) \]

\[ \rightarrow \text{Me}(g) + n\text{H}(g) \]

\[ \rightarrow \Sigma \text{IP} \rightarrow \text{EA} \]

\[ \rightarrow \text{Me}^{n+}(g) + n\text{H}^-(g) \]

\[ \rightarrow S \rightarrow nD \]

\[ \rightarrow \Delta H_f \rightarrow U_{pot} \]

Figure 4. Born-Haber cycle for the formation of solid binary metal hydride from solid metal and gaseous hydrogen

Applying Hess’ Law \( \Delta H_f \) is expressed by

\[ \Delta H_f = S + \frac{n}{2} D + \sum n \text{IP} + \text{EA} + U_{tot} \] (8)

where \( S \) is the sublimation enthalpy of the metal ion i.e. the energy required to transfer the solid metal to gaseous form, \( D \) is the dissociation enthalpy of the hydrogen molecule, \( IP \) is the ionization potential of the metal ion, \( EA \) is the electron affinity of the hydrogen atom and \( U_{tot} \) is the lattice enthalpy of the metal hydride. The summation of the ionization potential is required for polyvalent metal cations e.g. the total ionization potential of Mg is the summation of the 1. and 2. ionization potential (formation of Mg\(^+\) from Mg\(^0\) and subsequently formation of Mg\(^{2+}\) from Mg\(^+\)). From above we see that if all terms on the right hand side of eq. 8 is known \( \Delta H_f \) can be estimated. Tabulated values of \( S, D, IP \) and \( EA \) can be found in ref. [11].

The total crystal lattice energy \( U_{tot} \) when the ions are at their equilibrium positions can be estimated using the Born-Landé equation [13].

\[ U_{tot} = -\frac{N_A A z_+ z_- e^2}{4\pi\epsilon_0 R_0} \left( 1 - \frac{1}{n} \right) \] (9)

where \( N_A \) is the Avogadro number, \( A \) is the Madelung constant, \( z_+ \) and \( z_- \) is the number charge of the cation and anion, respectively, \( e \) is the electron charge, \( \epsilon_0 \) is the permittivity in vacuum, \( R_0 \) is the shortest separation between cation and anion centers and \( n \) is a repulsion coefficient.
We have used the Born-Haber cycle to predict the formation enthalpy of a number of binary hydrides based on alkali metals, alkaline earth metals, transition metals and rare earth metals. The calculational parameters are summarized in table 1. Also listed are the predicted values of $H_f$.

Predicted $H_f$ are compared with experimentally determined values in figure 5. As shown on the figure predicted values of the formation enthalpy for the alkali metal hydrides are in excellent agreement with experiments taken the simplicity of the model into account. This is not surprising due to the ionic like bonding in the alkali metal hydrides. The alkaline earth metal hydrides are less ionic in nature (the difference in electronegativity between the metal cation and the hydrogen anion is less than for the alkali metals). Thus, poorer agreement between calculations and experiment should be expected. According to figure 5 this is also the case. However, the Born-Haber cycle calculations performs well on a qualitative scale i.e. it predicts the correct order in thermodynamic stability: Ca being the most stable, Mg the least stable and Sr and Ba having roughly the same stability. When moving to the transition metals and the rare earth metals the Born-Haber predictions seem to break down due to a higher degree of metallic bonding character. Nonetheless, it still seem to have some limited applicability to the early transition metals forming hydrides under strongly exothermic conditions.

### Table 1. Parameters used in the Born-Haber cycle calculations and calculated $\Delta H_f$ for selected alkali metal hydrides, alkaline earth metal hydrides, transition metal hydrides and rare earth hydrides. All listed values are given in kJ/mol. Calculated values for $U_{tot}$ have been adapted from ref. [11].

<table>
<thead>
<tr>
<th>Metal hydride</th>
<th>$S$</th>
<th>$\sum_n IP$</th>
<th>$U_{tot}$</th>
<th>$\Delta H_f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiH</td>
<td>160</td>
<td>520</td>
<td>-920</td>
<td>-96</td>
</tr>
<tr>
<td>NaH</td>
<td>108</td>
<td>496</td>
<td>-808</td>
<td>-60</td>
</tr>
<tr>
<td>KH</td>
<td>90</td>
<td>419</td>
<td>-714</td>
<td>-61</td>
</tr>
<tr>
<td>RbH</td>
<td>81</td>
<td>403</td>
<td>-685</td>
<td>-57</td>
</tr>
<tr>
<td>CsH</td>
<td>79</td>
<td>376</td>
<td>-644</td>
<td>-45</td>
</tr>
<tr>
<td>MgH$_2$</td>
<td>147</td>
<td>2177</td>
<td>-2791</td>
<td>-104</td>
</tr>
<tr>
<td>CaH$_2$</td>
<td>178</td>
<td>1726</td>
<td>-2410</td>
<td>-144</td>
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<tr>
<td>SrH$_2$</td>
<td>164</td>
<td>1605</td>
<td>-2250</td>
<td>-119</td>
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<tr>
<td>BaH$_2$</td>
<td>180</td>
<td>1461</td>
<td>-2121</td>
<td>-118</td>
</tr>
<tr>
<td>ScH$_3$</td>
<td>378</td>
<td>4235</td>
<td>-5439</td>
<td>-237</td>
</tr>
<tr>
<td>TiH$_2$</td>
<td>473</td>
<td>1959</td>
<td>-2866</td>
<td>-72</td>
</tr>
<tr>
<td>VH</td>
<td>514</td>
<td>648</td>
<td>-1184</td>
<td>122</td>
</tr>
<tr>
<td>CrH</td>
<td>396</td>
<td>650</td>
<td>-1050</td>
<td>140</td>
</tr>
<tr>
<td>FeH$_3$</td>
<td>416</td>
<td>5255</td>
<td>-5724</td>
<td>536</td>
</tr>
<tr>
<td>NiH</td>
<td>430</td>
<td>733</td>
<td>-929</td>
<td>378</td>
</tr>
<tr>
<td>CuH</td>
<td>337</td>
<td>742</td>
<td>-828</td>
<td>395</td>
</tr>
<tr>
<td>ZnH$_2$</td>
<td>130</td>
<td>2626</td>
<td>-2870</td>
<td>249</td>
</tr>
<tr>
<td>LaH$_2$</td>
<td>431</td>
<td>1597</td>
<td>-2380</td>
<td>10</td>
</tr>
<tr>
<td>CeH$_2$</td>
<td>423</td>
<td>1573</td>
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<td>-56</td>
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<tr>
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<td>356</td>
<td>1537</td>
<td>-2448</td>
<td>-193</td>
</tr>
<tr>
<td>NdH$_2$</td>
<td>328</td>
<td>1560</td>
<td>-2464</td>
<td>-214</td>
</tr>
</tbody>
</table>

### 3.2 The Miedema model

Miedema and co-workers have proposed a semi-empirical model known as the *Miedema model* for the formation enthalpy of transition metal alloys and metallic alloys between transition metals and non-transition metals. The basis of the model
Figure 5. Predicted vs. experimental values for $\Delta H_f$ calculated from the Born-Haber cycle. Experimental determined $\Delta H_f$ for the alkali metal hydrides are from ref. [14], experimental $\Delta H_f$ for the alkaline earth metal hydrides are from ref. [15], experimental $\Delta H_f$ for the rare earth metal hydrides are from ref. [12] and experimental $\Delta H_f$ for the transition metals are from ref. [11, 15]. The full line represents the case when pred. equal exp.

is the Wigner-Seitz concept of atomic cells. For a detailed description of the model we refer to ref. [16, 17, 18, 19]. The Miedema model have also been extended to account for hydride formation enthalpies of binary metal hydrides [15, 19, 20].

The alloy formation can be described by the following reaction.

\[ yA + zB \rightarrow A_y B_z \]  

(10)

With $y$ and $z$ being the stoichiometric coefficients of $A$ and $B$, respectively. The enthalpy of formation of the alloy, $\Delta H_{A_y B_z}$, is given by:

\[ \Delta H_{A_y B_z} = \Delta H'_{A_y B_z} + y \Delta H_{trans}^A + z \Delta H_{trans}^B \]  

(11)

Assuming that $A$ and $B$ are metallic $\Delta H'_{A_y B_z}$ can be calculated by the Miedema formalism

\[ \Delta H'_{A_y B_z} = \frac{2f(c^*)c_A V_A^{2/3} + c_B V_B^{2/3}}{(n_{w_A}^{A})^{-1/3} + (n_{w_B}^{B})^{-1/3}} \times \left[ -P(\Delta \Phi^*)^2 + Q(n_{w_A}^{1/3})^2 - R \right] \]  

(12)

where $c_A$ and $c_B$ are atomic concentrations of elements $A$ and $B$, $V_A$ and $V_B$ are the molar volumes, $\Delta \Phi^* = \Phi_A^* - \Phi_B^*$ is the difference in electronegativity, $\Delta n_{w_A}^{1/3} = (n_{w_A}^{A})^{-1/3} - (n_{w_A}^{B})^{-1/3}$, where $n_{w_A}^{A}$ and $n_{w_B}^{B}$ are the electron densities of $A$ and $B$ at the boundary of their Wigner-Seitz cells, respectively, $Q$, $P$, and $R$ are constants, and $f(c^*)$ is a function of the atomic concentrations given by:

\[ f(c^*) = c_A^s c_B^s \left[ 1 + 8(c_A^s c_B^s)^2 \right] \]  

(13)

with

\[ c_A^s = \frac{c_A V_A^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \]  

(14)

\[ c_B^s = \frac{c_B V_B^{2/3}}{c_A V_A^{2/3} + c_B V_B^{2/3}} \]  

(15)

The $H_{trans}^A$ in eq. 11 is included to account for transformation from non-metallic to metallic state e.g. if $A$ is a metal and $B$ is hydrogen $\Delta H_{trans}^A$ is zero and $\Delta H_{trans}^B$
is non-zero since hydrogen is non-metallic in its ground state. The energy required
to transform gaseous hydrogen into metallic hydrogen have been estimated to
approx. 100 kJ/mol H [19]. The Miedema model have also been extended to predict
hydrogen content in binary hydrides of the form AH₂ [15]. This is simply done by
replacing \( y \) and \( z \) with \( 1/(1+x) \) and \( x/(1+x) \), respectively. The formation enthalpy
can now be written as:

\[
\Delta H_{AH_x} = (1 + x)\Delta H'_{A/(1+x)B_{x/(1+x)}}
\] (16)

The hydrogen content is now determined as the value of \( x \) giving the most stable
configuration i.e. the minimum enthalpy.

The performance of the Miedema model is evaluated by comparing predicted
values of the hydride formation enthalpies with experiments for a large number of
binary hydrides. This is shown in figure 6.

From the figure it is obvious that the Miedema model generally performs well
predicting the formation enthalpy of binary transition metal hydrides. This is consis-
tent with the picture drawn in ref. [19]. The model also perform well predicting
\( \Delta H_f \) for divalent rare earth hydrides. However, the formation enthalpy of the
trivalent rare earth hydrides seem to be under-predicted by approx. 100 kJ/mol.
Surprisingly, the model also does a good job (except for Be) predicting the for-
mation enthalpy of the alkaline earth metal hydrides. This could suggest that the
bonding character in these compounds are in fact less ionic than suggested by the
Born-Haber calculations in the previous section. The Miedema model generally
under predicts the formation enthalpy of the alkali metal hydrides by approx. 75
kJ/mol H₂.

### 3.3 Advanced methods

In the previous sections we have had our focus on simple empirical models. While
attractive due to the fact that they offer estimates of formation enthalpies with
only little computational effort, the level of detail is limited. In this section we will
turn our focus towards more advanced methods with emphasis on EMT (Effective
Medium Theory) calculations and DFT (Density Functional Theory) calculations.
Figure 7. Heats of solution of hydrogen in transition metals. Filled circles are calculated values, Open squares are experimental values and open triangles the contribution to the heat of solution from $\Delta E_{\text{hom}}^{\text{eff}}$. The interstitial positions hosting the hydrogen atom are chosen as tetrahedral in BCC metals and octahedral in FCC and HCP metals. All values are extracted from ref. [21, 22].

Effective Medium Theory

The Effective Medium Theory was originally developed by Nørskov and co-workers and applied to the calculation of binding energies of small atoms in metals. EMT offers a simplified way of calculating total energies in contrast to ab initio methods. In EMT the surroundings of an embedded atom (in this case hydrogen) is approximated by a homogeneous electron gas. The total energy for embedding a hydrogen atom in position $\mathbf{R}$ into a transition metal can be expressed by the following summation

$$
\Delta E(\mathbf{R}) = \Delta E_{\text{hom}}^{\text{eff}}(\tilde{n}_0(\mathbf{R})) + \Delta E_c(\mathbf{R}) + \Delta E_v(\mathbf{R}) + \Delta E_{\text{hyb}}(\mathbf{R})
$$

(17)

where $\Delta E_{\text{hom}}^{\text{eff}}(\tilde{n}_0(\mathbf{R}))$ describes the interaction between the embedded hydrogen atom and the homogeneous electron gas with electron density $\tilde{n}_0$, $\Delta E_c(\mathbf{R})$ is a correction term describing interaction between the metal cores and the hydrogen atom. $\Delta E_v(\mathbf{R})$ is a correction term dependent on the definition of $\Delta E_{\text{hyb}}(\mathbf{R})$. $\Delta E_{\text{hyb}}(\mathbf{R})$ is a hybridization term describing hybridization between hydrogen and the metal $d$ electrons. For a more detailed description of the basis and applications of EMT we refer to ref. [21, 22, 23, 24] and references within.

When calculating $\Delta E(\mathbf{R})$ typically an appropriate unit cell of the host metal metal is chosen with finite size. The total electronic energy is then evaluated by inserting $n$ H atoms in the metal host. The formation enthalpy is evaluated by

$$
\Delta H_f = E_{\text{metal+H}}^{\text{tot}} - E_{\text{metal}}^{\text{tot}} - \frac{n}{2} E_{\text{H}_2}^{\text{tot}}
$$

(18)

with $E_{\text{metal+H}}^{\text{tot}} = \Delta E(\mathbf{R})$. If $n$ is small (= 1) the heat of solution is evaluated and if $n$ is large (close to the stoichiometry of the hydride) the hydride formation enthalpy is evaluated.

Nørskov and co-workers [21, 22] have used EMT to calculate the heat of solution of hydrogen in 27 3d, 4d and 5d transition metals. The result is shown in figure 7. From the figure it is noticed that the EMT generally does a good job predicting the trend in heats of solution of hydrogen in transition metals. However, the early and late transition metals seem to be under and over predicted, respectively by the model. There are also other interesting properties: i) There is a tendency for
<table>
<thead>
<tr>
<th></th>
<th>Heat of solution [kJ/mol H]</th>
<th>Heat of formation [kJ/mol H]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>29</td>
<td>27</td>
</tr>
<tr>
<td>Pd</td>
<td>-12</td>
<td>-16</td>
</tr>
<tr>
<td>Pt</td>
<td>25</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 2. Heats of solution and heats of hydride formation of Ni, Pd and Pt determined by EMT-calculations and compared with experiments. All data are read graphically from ref. [23]. The calculated values have not been corrected with thermal or zero point energies. In the case of Pd the calculated energy should be reduced by approx. 7 kJ/mol by doing so [23].

stronger binding to the left in the periodic table

\( \text{ii) The variation in the heat of solution is more or less governed by changes in } \Delta E_{\text{hom}}^{\text{eff}}(\hat{n}_0(R)). \) \( \Delta E_{\text{hom}}^{\text{eff}}(\hat{n}_0(R)) \) is roughly proportional to the electron density. \( \text{ii) The heats of solution show a broad maximum near the middle of the transition metal series. This may be accounted for by the fact that the electron density shows a maximum around the middle of the transition metals where the } d \text{-band is half filled (this is reflected in a maximum in } \Delta E_{\text{hom}}^{\text{eff}}(\hat{n}_0(R))). \)

Christensen et al. [23] calculated both heats of solution of hydrogen in Ni, Pd and Pt and heats of formation of the corresponding hydrides. The results of their calculations are summarized in table 2 together with experimental determined values.

From table 2 it is observed that despite the crudeness of the calculations experimental values are successfully reproduced. More important is the fact that the model predicts the trend that H in Ni is endothermic (and probably also in Pt) while H in Pd is endothermic. The reason for this may be accounted for by considering the difference in interstitial electron density in the two metals. Ni has a smaller lattice constant (3.52 Å) compared to Pd (3.89 Å) and thereby a larger interstitial electron density. This is reflected in a higher heat of solution and a higher heat of formation, respectively, due to the \( \Delta E_{\text{hom}}^{\text{eff}}(\hat{n}_0(R)) \) contribution in eq. 17. Based on total energy calculation at varying hydrogen content the authors propose that the fact the hydride phase is stable with hydrogen content above \( x = 0.6 \) is due to the level off in H-H attractions.

Density Functional Theory

The Hamiltonian, \( H \), of a system with N electrons and M nuclei under the Born-Oppenheimer approximation is

\[
H = \sum_{i} \left( -\frac{1}{2} \nabla_i^2 + \frac{1}{2} \sum_{i<j} \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} - \sum_{i,l} \frac{Z_l}{|\mathbf{r}_i - \mathbf{R}_l|} + \sum_{k<l} \frac{Z_l Z_k}{|\mathbf{R}_k - \mathbf{R}_l|} \right)
\]

where \( \mathbf{r} \) and \( \mathbf{R} \) are the coordinates of the electrons and nuclei, respectively. The first term is the kinetic energy operator for the electrons, the second term is the electron-electron repulsion, the third and fourth term are the electron-nucleus and nucleus-nucleus interactions, respectively.

Wave function methods such as Hartree-Fock (HF) and configuration interaction (CI) try to determine the N-electron eigenfunction to the Schrödinger equation corresponding to the Hamiltonian (Eq. 19) under the constraint of antisymmetry with respect to interchange of two electrons. Density Functional Theory (DFT) takes a fundamentally different approach. In DFT the fundamental variable is not
the wave function, but the corresponding observable electron density, \( n(\mathbf{r}) \)

\[
n(\mathbf{r}) = \sum_{\sigma} d\sigma \int d\mathbf{x}_2 \cdots \int d\mathbf{x}_N |\psi(\mathbf{r}, \mathbf{x}_2, \ldots, \mathbf{x}_N)|^2, \tag{20}
\]

where the integrals over \( \mathbf{x}_i \) denote sums over the spin coordinates \( \sigma_i \) and integrals over the space coordinates \( \mathbf{r}_i \). Hohenberg and Kohn \[25\] proved that the total energy of a system of interacting electrons is a unique functional of the electron density. It was further proven that the ground state density minimizes the functional (variational principle). Hence it is possible to obtain the ground state total energy of the system by minimizing the total energy, \( E[n(\mathbf{r})] \), with respect to the electron density under the constraint that the particle number is conserved. The theorems imply that the original 3N dimensional problem of finding the N-electron wave functions can in principle be reduced to a 3 dimensional problem of finding the density.

Kohn and Sham \[26\] wrote the energy functional as

\[
E[n] = T_0[n] + \int d\mathbf{r} n(\mathbf{r}) V_{ex}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} n(\mathbf{r}) \int d\mathbf{r}' \frac{n(\mathbf{r}')}}{|\mathbf{r} - \mathbf{r}'|} + E_{xc}[n], \tag{21}
\]

where \( T_0[n] \) is the exact kinetic energy of N non-interacting electrons with the density \( n \). \( E_{xc} \) is termed the exchange-correlation energy, and is the only term not known exactly.

Solving the Kohn-Sham equations \[26\]

\[
\left(-\frac{1}{2} \nabla^2 + \nu\right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \tag{22}
\]

with the constraint

\[
\sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 = n(\mathbf{r}) \tag{23}
\]

the kinetic energy of the non-interacting electron gas, \( T_0[n(\mathbf{r})] \), is obtained as

\[
T_0[n(\mathbf{r})] = \sum_{i=1}^{N} \epsilon_i + \int \nu(\mathbf{r}) n(\mathbf{r}) d\mathbf{r} \tag{24}
\]

\( \nu \) is the effective one-electron potential and the ground state is given by

\[
\nu(\mathbf{r}) = \phi(\mathbf{r}) + \nu_{ex}(\mathbf{r}) \tag{25}
\]

where \( \phi(\mathbf{r}) \) is the electrostatic potential

\[
\phi(\mathbf{r}) = \nu_{ex}(\mathbf{r}) + \int \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}' \tag{26}
\]

and the exchange and correlation potential is defined as

\[
\nu_{xc}(\mathbf{r}) = \frac{\delta E_{xc}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \tag{27}
\]

By solving Eq. 22 and 22 self-consistently the ground state energy \( E_0 \) and density \( n_0 \) can be obtained. The problem has been reduced to solving a system of N non-interacting electrons. The above procedure is in principle exact, but approximations will enter because \( E_{xc}[n(\mathbf{r})] \) is not known explicitly. \( E_{xc}[n(\mathbf{r})] \) contains the many-body complications. For additional details about exchange-correlations, \( k \)-point sampling, cut-off energy etc. we refer to ref. \[26, 27, 28, 29, 30, 31\].

The literature contains many examples of the application of DFT to binary metal hydrides. However, in brief we will only use a few representative examples.
Yu and Lam have studied the electronic and structural properties of MgH$_2$ using DFT [32]. Assuming the experimentally stable rutile structure of MgH$_2$ they minimized the total energy by optimizing the lattice parameters. The calculated equilibrium values agreed to within 2.2 % of the experimentally determined values. Analysis of the electronic properties show that MgH$_2$ is an insulator with a band gap of 3.06 eV. However, this is 2 eV lower than the experimentally determined band gap. The cohesive energy is found to be 11.2-13.5 eV (exp. 13.56 eV). From this the enthalpy of formation of magnesium hydride is approximated to be between $\Delta H_f = -38.4$ kJ/mol H$_2$ to $\Delta H_f = -72$ kJ/mol H$_2$ (exp. $\Delta H_f \approx -75$ kJ/mol H$_2$). The discrepancy between theory and experiment may probably be assigned to the choice of the LDA (Local Density Approximation) exchange-correlation.

Both Miwa and Fukumoto [33] and Smithson et al. [34] made first principles study of the interaction of hydrogen with transition metals within the DFT formalism. While Miwa and Fukumotos investigation is restricted to Ti, V, Cr, Fe and Ni Smithson et al. have calculated formation energies for all 3$d$ and 4$d$ transition metal hydrides. Despite the use of different exchange-correlations (Miwa and Fukumoto use GGA while Smithson et al. use LDA) the authors reach quite similar conclusions. It is generally found that the early transition metals form stable hydrides and that the formation enthalpy is rapidly lowered when moving to the right in the transition metals. Around the middle this trend levels off and a slight increase in the formation energy is found when moving further to the right [33, 34]. To the far right (noble metals) a huge increase in the formation energy is found implying that these hydrides are unstable [34]. This is all illustrated for dihydrides with the CaF$_2$ structure by the full line in figure 8. Furthermore, $\Delta H_f$ may be decomposed into the following three parts [33, 34]

$$\Delta H_f = E_{\text{transform}} + E_{\text{expansion}} + E_{\text{hydride}}$$

(28)

where $E_{\text{transform}}$ is the energy required in order to transform the host metal lattice into the arrangement of the metal ions in the metal hydride, $E_{\text{expansion}}$ is the energy required to expand the host metal lattice to that of the hydride and finally $E_{\text{hydride}}$ is the hydrogen insertion energy in the expanded metal lattice.

Figure 8. Trend in formation enthalpy for 3$d$ transition metal dihydrides with the CaF$_2$ structure (full line). The red bars represent $E_{\text{hydride}}$, blue bars represent $E_{\text{transform}}$ and green bars represent $E_{\text{expansion}}$. All data points are adapted from ref. [34].
<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>$\Delta H_f$(DFT) [kJ/mol H]</th>
<th>$\Delta H_f$(Exp) [kJ/mol H]</th>
<th>Ref.</th>
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<td>LaH$_3$</td>
<td>BiF$_3$</td>
<td>-78</td>
<td>-82.5</td>
<td>[15]</td>
</tr>
</tbody>
</table>

Table 3. Formation enthalpies for binary metal hydrides from DFT-calculations and experiments. All calculated values are from ref. [35].

three contributions are also mapped in figure 8.

From figure 8 we note that the lattice expansion energy $E_{\text{expansion}}$ increases from the left until Fe and subsequently decreases. This may be explained from the cohesion energy which have its maximum around the middle of the transition metals where the $d$-band is half filled and decreases when the $d$-band filling is higher and lower, respectively. The structural transformation energy $E_{\text{transform}}$ is low when host metal structure is close to that of the hydride. This is the case for more or less most of the metals except for V and Cr which have stable bcc structures. The remaining contribution to $\Delta H_f$ is $E_{\text{hydride}}$ and this is by far the most important contribution. We note that the trend in $E_{\text{hydride}}$ is directly reflected in the trend for $\Delta H_f$. Miwa and Fukumoto [33] suggested a simple relation between the hydrogen insertion energy and the interstitial hole size in the metal lattice of the following form

$$E_{\text{hydride}} = \alpha R^{-\beta}$$

(29)

where $\alpha$, $n$ and $\beta$ are fitting parameters and $R$ is the hydrogen-metal interatomic distance. The above relation implies that the larger the interstitial hole size the more energetically favorable is the hydrogen insertion.

Smithson et al. also performed total energy DFT-LDA calculation for the hydrides of the alkali metals and the alkaline earth metals [34]. In the case of the alkali metal hydrides all adopt the NaCl structure and calculations qualitatively predicted the trend in hydride stability. However, the calculations generally seemed to over predict the stability. For the alkaline earth metals the correct structure of the hydrides are predicted (rutile for MgH$_2$ and Co$_2$Si for Ca, Sr, Ba). However, quantitatively the enthalpy of formation is only within 50 kJ/mol of experimentally observed values.

To test the performance in general of DFT as a method of predicted $\Delta H_f$ we use the results of Wolverton et al. [35] who performed calculations of a number of selected alkali, alkaline earth and transition metal hydrides using DFT-GGA. We believe that GGA exchange-correlation generally performs better than LDA. Further, the description of gas phase H$_2$ and vibrational entropy contributions

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from the solid state phases by Wolverton et al. seems more realistic than that of Smithson et al.

The results of the calculations of Wolverton et al. are summarized in table 3 along with experimental values. As also shown in the table the structure of the hydride is also given and the selected metal hydrides cover not only many different kinds of metals but also many different kinds of structures with different kinds of environments for inserted hydrogen atoms. The agreement between calculations and experiment is also summarized in figure 9. The agreement between calculations and experiment is generally quite good. The DFT-GGA calculations are superior to Born-Haber cycle calculations cf. figure 5 and also better than the Miedema model cf. figure 6. Direct comparison with the EMT calculations cf. 7 is difficult since only transition metals are dealt with using this method. However, on a more specific basis the DFT-GGA calculations seem to under predict the stability of the alkali metal hydrides but not as bad as the Miedema model. Besides this discrepancy it performs excellent predicting $\Delta H_f$ for both alkaline earth metal hydrides and transition metal hydrides including the di- and tri hydride of La.
4 Ternary hydrides

Until now we have had our focus on the binary metal hydrides and experimental results of the enthalpy of hydride formation show that these cover a wide range in stability going from the highly stable hydrides ($\Delta H_f < 0$) of the alkali metals, alkaline earth metals, rare earth metals and early transition metals to the much less stable hydrides of the metal hydrides around the middle of the transition metals ($\Delta H_f < 0$) towards the unstable hydrides of the late transition metals ($\Delta H_f > 0$). As mentioned previously the criterion for the formation enthalpy was $\Delta H_f > -48 \text{ kJ/mol H}_2$. This should easily be met by a proper choice of binary metal hydride. However, if the energy density criterion should also be met the task may not seem that easy. In figure 10 the gravimetric hydrogen density $\rho_{H_2}(\text{m})$ is plotted as a function of $\Delta H_f$ for most the binary metal hydrides investigated so far. From the figure it is obvious that none of the metal hydrides fulfill both the hydrogen density criterion and the thermodynamic stability criterion. This is of course old news and as a natural consequence the search for better hydrogen storage materials continue among the ternary metal hydrides.

![Figure 10. Relationship between the gravimetric hydrogen density and the experimentally observed formation enthalpy [15] of selected binary hydrides of alkali metals, alkaline earth metals, transition metals and rare earth metals.](image)

4.1 A simple model

In order to develop a simple empirical model for $\Delta H_f$ of ternary hydrides we shall examine the effect of *alloying* two binary metal hydrides. In figure 11 A-D $\Delta H_f$ for LaNi$_5$H$_6$, Mg$_2$NiH$_4$, TiFeH$_2$, and Mg$_2$FeH$_6$ are shown along with $\Delta H_f$ for their binary hydride constituents. Each plot is organized in the following manner: placed to left is the metal forming the most stable hydride e.g. for LaNi$_5$ it is La, in middle we have the ternary hydride and placed to the right is the metal forming the least stable hydride e.g. for LaNi$_5$ this is Ni.

According to figure 11 A-C $\Delta H_f$ of the ternary hydride is somewhere in between that of the two binary hydride constituents. This is in fact also the case for many

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2 This term is purely used for illustrational reasons. In practice the ternary hydride is often formed by first alloying the metal constituents and then subsequently hydriding the metal alloy into a ternary hydride.

3 Whenever Fe appears the bar representing $\Delta H_f$ seems to be missing. This is not an error,
Figure 11. Enthalpy of formation of ternary hydrides and compared to their corresponding binary hydrides. A: LaH$_2$, LaNi$_5$H$_6$ and NiH [12, 5, 15], B: MgH$_2$, Mg$_2$NiH$_4$ and NiH [15, 36, 37], C: TiH$_2$, FeTiH$_2$ and FeH [38, 5, 15], D: MgH$_2$, Mg$_2$FeH$_6$ and FeH [15, 36, 37]

other ternary hydrides e.g. ZrCr$_{1.8}$, TiCr$_{1.8}$, ZrMn$_2$, ZrNi, CaNi$_5$, NaAlH$_5$, LiBH$_4$ (cf. figure 3, table 5 and ref. [5, 15, 12]). From the figure we note that the effect of alloying with Ni has the largest effect (more pronounced lowering $\Delta H_f$) of LaNi$_5$ compared to Mg$_2$Ni. This suggests that $\Delta H_f$ of the ternary hydride is related to stoichiometry of the two host metals. Thus increasing the amount of weakly hydride forming metal reduces $\Delta H_f$ of the alloy. We propose the following model for $\Delta H_f$ of a ternary metal hydride $AB_xH_y$ as a weighted average of $\Delta H_f$ for the binary metal hydrides

$$\Delta H_f(A_xB_yH_{u+v}) = \frac{x}{x+y} \Delta H_f(AH_u) + \frac{y}{x+y} \Delta H_f(BH_v)$$

(30)

based on the following general reaction equation describing alloying of two binary metal hydrides

$$xAH_u + yBH_v = A_xB_yH_{u+v}$$

(31)

By convention $A$ refers to the metal forming a the most stable hydride and $B$ refers to the weakly hydride forming metal (compared to $A$).

Equation 30 explicitly states that $\Delta H_f$ of the ternary hydride can be modified by either changing $\Delta H_f(AH_u)$ or $\Delta H_f(BH_v)$ by substitution e.g. the less stable $BH_v$ is the less stable will the ternary hydride be. However, according to figure 11 B and D when substituting Ni with Fe in Mg-alloys the opposite is observed experimentally clearly indicating a limitation in the model. Further, experimental observations suggests that replacing La in LaNi$_5$ with another rare earth metal e.g. Pr or Ce the stability of the ternary hydride decrease in the following order LaNi$_5$ but due to the fact that $\Delta H_f$ for iron hydride is close to zero or even slightly positive.
Figure 12. Schematic of the hydrogen positions in $AB_n$ alloys. To the top left is shown an alloy poor in component A (hydride forming). Below is the corresponding hydride. To the lower right an $AB$ ($n=1$) type alloy rich in A is shown with its corresponding allow (above). Adapted from ref. [19, 39].

> PrNi$_2$ > CeNi$_5$ [5]. However, $\Delta H_f$ of the rare earth metal hydrides increase in the following manner LaH$_2$ < PrH$_2$ < CeH$_2$ [15]. Thus, according to eq. 30 the opposite trend in $\Delta H_f$ of ReNi$_5$ is predicted. Again the model shows clear limitations. Henceforth a better suited model is called upon.

### 4.2 The rule of reversed stability

Miedema and coworkers have proposed a model to predict $\Delta H_f$ for ternary hydrides [19, 39]. This model is also known as the rule of reversed stability (which become clear in moment) and $\Delta H_f$ of the ternary hydride ($AB_nH_{x+y}$) is given by

$$\Delta H_f = \Delta H(AH_x) + \Delta H(B_nH_y) - \Delta H(AB_n)$$  \hspace{1cm} (32)

where A is a transition metal forming a stable hydride e.g. Sc, Y, La, Ti, Zr, Hf, Th, U, and Pu, $B$ is an arbitrary transition metal, $\Delta H(AH_x)$ is the heat of formation of the hydride of A, $\Delta H(B_nH_y)$ is the heat of formation of the hydride of $B$, and $\Delta H(AB_n)$ is the heat of formation of the $AB_n$ alloy. According to eq. 32 the more stable an alloy A and B forms the less stable will the corresponding hydride be, hence the name of the model. This feature is the only difference between this model and the simple model proposed in the previous section i.e. $\Delta H_f$ is also proportional to the heat of formation of the binary hydrides of A and B.

The input to the model is either experimentally known heats of formation of the binary hydrides of A and B and heat of formation of the $AB_n$ alloy or estimated values using the Miedema model described previously. The basis of the model is the assumption that the bonds/contacts between neighboring A and B atoms are at least partially broken upon hydrogenation due to hydrogen surrounding A atoms. This is shown in figure 12.1.

Relation 32 only holds for compounds with large $n$ corresponding to figure 12.1 where all contacts between A and B atoms are broken due to insertion of hydrogen e.g. LaNi$_5$. In order to have more general applicability viz. for smaller values of $n$
Table 4. Formation enthalpies for binary metal hydrides from DFT-calculations and experiments. All calculated values are from ref. [35].

<table>
<thead>
<tr>
<th>Metal A</th>
<th>$AB_n$</th>
<th>$AB_nH$</th>
<th>$x$</th>
<th>$y$</th>
<th>$F$</th>
</tr>
</thead>
<tbody>
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<td>$AB_5H_5$</td>
<td>2</td>
<td>3</td>
<td>0.1</td>
</tr>
<tr>
<td>V, Nb, Ta, Sc</td>
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<td>$AB_3H_4$</td>
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<td>2</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>$AB_2$</td>
<td>$AB_2H_{3.5}$</td>
<td>2</td>
<td>2.5</td>
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</tr>
<tr>
<td></td>
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<td>$ABH_2$</td>
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<td>0.6</td>
</tr>
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<td>0.1</td>
</tr>
<tr>
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<td>$AB_3H_5$</td>
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<td>2</td>
<td>0.5</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Figure 13. Predicted values of the formation enthalpy of intermetallic ternary hydrides obtained from Miedema model calculations [19] and the rule of reversed stability vs. experimental values [5, 15].

(but still $n \geq 1$) \(32\) is modified to

$$\Delta H_f = \Delta H(\text{AH}_x) + \Delta H(B_nH_y) - (1 - F)\Delta H(AB_n) \tag{33}$$

where $F$ varies with alloy composition, \(n\): the more rich in $B$ (small $n$) the larger value of $F$ in order to compensate for the fact that not all bonds between $A$ and $B$ atoms are broken upon hydrogenation if $n$ is small cf. figure 12.2. Miedema and coworkers have proposed the values of $F$ shown in table 4 along with values of $n$ and $m$.

In order to validate we model we inspect model predictions versus experimentally determined values of $\Delta H_f$. The model predictions are based on the rule of reversed stability with enthalpy of formation of both $A$ and $B$ hydrides and the $AB$ alloy calculated from the Miedema model [19]. This is shown in figure 13 where the data of the hydrides of 9 $AB$, 12 $AB_2$, 1 $AB_3$, and $AB_5$ compounds are plotted. From the figure we note that the data points of $\Delta H_f$ seem to be more scattered for the ternary hydrides than for the binary hydrides using the Miedema model. This suggest that the increased scatter is introduced by the rule of reversed stability. With the rule of reversed stability initially being derived for large values of $n$ it is perhaps not that surprising to see that the model does a reasonable job with the $AB_n$ hydrides (with exception of LaPt$_5$).

\(^{4}\)The estimated value of $\Delta H_f$ for LaPt$_5$ was based on only one reported plateau pressure [5] and assuming $\Delta S = -190 J/(mol \cdot K)$. Thus even moderate experimental inaccuracies may effect...
ity seems to generally over predict the value of $\Delta H_f$ hence predicting too stable ternary hydrides. Besides this trend the deviations from experiments seem to be rather unsystematic.

### 4.3 DFT

Unfortunately the literature on DFT applied to intermetallic hydrides is sparse. Due to this fact we will focus on two distinct group of hydrides: the magnesium based hydrides (hydrides of magnesium alloys) and the complex hydrides (alanates and borohydrides e.g. NaAlH$_4$ and LiBH$_4$).

**Magnesium based hydrides**

For simplicity we will in the following focus on the hydrogenation behavior of the Mg 3$d$ transition metal alloys.

Magnesium is known to form an Mg$_2$Cu [40] alloy which disproportionates to magnesium hydride and MgCu$_2$ upon hydrogenation [41, 42].

\[
2Mg_2Cu + 3H_2 \rightleftharpoons 3MgH_2 + MgCu_2
\]

(34)

From experiments $\Delta H_f$ have been reported to be approx. -70 kJ/mol $H_2$ (5 kJ/mol lower than for pure Mg).

Magnesium is also known to form a stable Mg$_2$Ni alloy [40] which forms a complex Mg$_2$NiH$_2$ hydride [5].

\[
Mg_2Ni + 2H_2 \rightleftharpoons Mg_2NiH_4
\]

(35)

$\Delta H_f$ is approx. -62 kJ/mol $H_2$ [36, 5].

Magnesium does not form an alloy with Co. However applying ball milling sintering under hydrogen atmosphere produces a complex hydride [43] with $\Delta H_f$ of approx. 76 kJ/mol $H_2$ [36].

\[
2Mg + Co + \frac{5}{2}H_2 \rightleftharpoons Mg_2CoH_5
\]

(36)

A compound more rich in magnesium (Mg$_6$CoH$_{11}$) have also been reported with $\Delta H_f = -89$ kJ/mol $H_2$

Magnesium does not form a stable Mg-Fe alloy either (calculations using the Miedema model shows a positive formation enthalpy for the formation of both Mg-Co and Mg-Fe [15]). Applying ball milling under hydrogen atmosphere produces a complex hydride [43] $\Delta H_f$ is approx. -77 kJ/mol $H_2$ [36].

\[
2Mg + Fe + 3H_2 \rightleftharpoons Mg_2FeH_6
\]

(37)

Magnesium and manganese have shown to form a complex hydride. However, only if applying very high pressure of hydrogen ($\approx 20$ kbar) and high temperature ($\approx 700^\circ C$) [44]

\[
3Mg + Mn + \frac{7}{2}H_2 \rightleftharpoons Mg_3MnH_7
\]

(38)

The compound decomposes around 280 $^\circ C$. Assuming $\Delta S = -130$ J/(mol K) $\Delta H_f$ can be estimated to be approx. -72 kJ/mol H$_2$.

Vegge et al. [45] have investigated the trends in hydride formation of the MgTM alloys where TM is 3$d$-transition metal belonging to the group Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn using DFT calculations. The authors use a body centered tetragonal unit cell for the MgTM structure with TM in the body center which is the value of $\Delta H_f$ significantly.

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Figure 14. A schematic representation of the MgFeH$_3$ hydride in the Perovskite structure. Magnesium atoms at the corners (green), an iron atom in the center (orange), and hydrogen atoms at face centers (white). Figure is adapted from ref. [45].

![Figure 14](image1.png)

Figure 15. Trend in $\Delta H_f$ of the MgTM alloys. Calculated values are from [45] and experimental values of Fe, Co, and Ni are from [36]. Mn is estimated from [44].

![Figure 15](image2.png)

Initially relaxed. Sc, Co, Ni, and Cu relaxes in a bcc structure whereas the others remain tetragonal. For the hydrides a Perovskite structure is applied cf. figure 14 with the stoichiometry MgTMH$_3$ which remains cubic even after relaxation. The formation of hydride proceeds through the following reaction

$$MgTM + \frac{3}{2}H_2 \rightarrow MgTMH_3$$

For each of the MgTM hydrides the formation enthalpy is evaluated and the result is depicted in figure 15. The following trend in $\Delta H_f$ is observed: a gradual increase in the stability of the hydrides is observed going from MgSc to MgFe, which is followed by a rapid decrease in stability, resulting in MgNiH$_3$ hydride being only marginally stable and MgCuH$_3$ and MgZnH$_3$ unstable. The results are compared with literature data for $\Delta H_f$ of known MgTM hydrides as reviewed above. The experimental trend is the following: Mg$_2$Fe hydride is most stable thus stability decreases going both left to Mn and right towards Co and Ni. Mg$_2$Ni hydride is the least stable hydride. Despite the fact that the calculated values are...
based on a different stoichiometry of both the MgTM alloys and the corresponding hydrides, respectively, compared to experimental observation (and thus different structure) the trend found using DFT resembles that of experiments. Although some shift in $\Delta H_f$ is observed probably due to differences in structure and stoichiometry. The fact that MgCu hydride is found unstable is also in agreement with experiments [41, 42]. Clearly DFT calculations are very useful in predicting trends in formation enthalpy of ternary metal hydrides.

### Complex hydrides

The complex hydrides in particular the alanates and borohydrides with the general formula $ABH_4$, where $A$ represents a metal (often an alkaline or an alkaline earth metal) and $B$ represents either aluminum or boron, is perhaps some of the most promising materials for hydrogen storage.

For sodium aluminum hydride the decomposition is a multi step mechanism

\[
(i) \quad NaAlH_4 \rightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2
\]

\[
(ii) \quad \frac{1}{3}Na_3AlH_6 \rightarrow NaH + \frac{1}{3}Al + \frac{1}{2}H_2
\]

\[
(iii) \quad NaH \rightarrow Na + \frac{1}{2}H_2
\]

\[
(i + ii) \quad NaAlH_4 \rightarrow NaH + Al + \frac{3}{2}H_2
\]

\[
(i + ii + iii) \quad NaAlH_4 \rightarrow Na + Al + 2H_2
\]

Until recently this process was regarded as irreversible. However, in 1997 Bogdanović and Schwickardi showed that adding a Ti-compound catalyzed the reaction and thereby making it reversible [47]. The maximum hydrogen capacity of NaAlH$_4$ is 7.5 wt. %. However, this requires dehydrogenation of NaH which is very stable (decomposes around 425 °C [11]). Thus high temperature must be applied in order to achieve full dehydrogenation. For practical applications NaAlH$_4$ should only be dehydrogenated to Na$_3$AlH$_6$ (reaction $i + ii$) releasing 3.7 wt. % and 1.9 wt. % hydrogen respectively resulting in a theoretical reversible capacity of 5.6 wt. % hydrogen. In practice a lower reversible capacity should be expected. The plateau pressure of reactions $i$ and $ii$ have been reported to be 1 bar at approx. 33°C and 110°C, respectively [46] cf. figure 16. NaAlH$_4$ is very close in fulfilling the criterions formulated by the USDOE. This is the reason for the extensive reasearch effort devoted to complex hydrides and in particular NaAlH$_4$ including DFT calculations on the heat of formation of the hydrides.

Calculated heats of formation is indeed advantageous since the acquisition of thermodynamic parameters from experiment (PCI/Van’t Hoff plot) is extremely tedious for the complex hydrides due to slow kinetics and limited reversibility. In table 5 calculated (DFT) heats of formation of the alkali alanates and alkali borohydrides, respectively, are compared with experimentally determined values either from calorimetric measurements or from PCI data. The values in table 5 are heats of formation of the hydrides from the elements in their standard states viz.

\[
Na(s) + Al(s) + 2H_2(g) \rightarrow NaAlH_4(s)
\]

and

\[
3Na(s) + Al(s) + 3H_2(g) \rightarrow Na_3AlH_6(s)
\]

In the literature a heat of reaction is often reported instead e.g. for reaction $i$ and/or reaction $ii$. In order to back calculate the heat of formation of the hydrides
as outlined above tabulated values of $\Delta H_f$ of the alkaline metal hydrides have been used [11].

From table 5 we note that there is generally excellent agreement between measured and calculated values of the alanates viz. $\text{MAH}_4$. Unfortunately experimental information about the stability of $\text{M}_3\text{AlH}_6$ is sparse. However, for $\text{Na}_3\text{AlH}_6$ the agreement between experiment and theory is fairly good. The general agreement between experiment and calculation gives reason to believe that the calculated heats of formation of $\text{Li}_3\text{AlH}_6$ and $\text{K}_3\text{AlH}_6$ are indeed qualified estimates. For the borohydrides only experimentally determined values are available for the $\text{MBH}_4$ and not for $\text{M}_3\text{AlH}_6$ compounds. For $\text{MBH}_4$ calculations seem to agree with experiments. According to table 5 the reaction enthalpy of decomposition of $\text{MAH}_4$ (reaction $i + ii$, $\Delta H(\text{MAH}_4) - \Delta H(\text{MH})$) and thus the decomposition temperature increase in the following sequence $\text{Li} < \text{Na} < \text{K}$. This is in agreement with experimentally observed decomposition temperatures [14, 48]. This is also the case for the borohydrides [11]. The most striking difference between the alanates and the borohydrides is the fact that the borohydrides are much more stable than the corresponding alanates [11, 14, 48]. This is also captured by the heats of formation obtained using DFT calculations.

It is interesting to note that none of the $\text{M}_3\text{BH}_6$ compounds are stable compared to their alkali metal metal hydride counterparts i.e. $\text{LiH}$, $\text{NaH}$ and $\text{KH}$. This suggests that the decomposition of the borohydrides is likely different from the scheme outlined by reactions $i - iii$ [49, 50].

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{van_t_hoff_plot.png}
\caption{Van’t Hoff plot for $\text{NaAlH}_4$. The stable hydride for each region of temperatures and pressures is marked on the graphic. Data points are taken from ref. [46].}
\end{figure}
### Alanates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Experimental</th>
<th>Theory</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiAlH₄</td>
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<td>-113-(-107)</td>
<td>[51, 52, 53, 49]</td>
</tr>
<tr>
<td>NaAlH₄</td>
<td>-115-(-109)</td>
<td>-116-(-113)</td>
<td>[51, 54, 46]</td>
</tr>
<tr>
<td>KAlH₅</td>
<td>-166</td>
<td>-151-(-150)</td>
<td>[51, 53, 49]</td>
</tr>
<tr>
<td>Li₃AlH₆</td>
<td>—</td>
<td>-311-(-305)</td>
<td>[52, 53, 49]</td>
</tr>
<tr>
<td>Na₃AlH₆</td>
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<td>-246-(-240)</td>
<td>[54, 46, 35, 53, 49]</td>
</tr>
<tr>
<td>K₃AlH₆</td>
<td>—</td>
<td>-276</td>
<td>[49]</td>
</tr>
</tbody>
</table>

### Borohydrides

<table>
<thead>
<tr>
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<th>Experimental</th>
<th>Theory</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
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<td>-180</td>
<td>[51, 49]</td>
</tr>
<tr>
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<td>-198</td>
<td>[51, 49]</td>
</tr>
<tr>
<td>KBH₄</td>
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<td>-216</td>
<td>[51, 49]</td>
</tr>
<tr>
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<td>-54</td>
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</tr>
<tr>
<td>K₃BH₆</td>
<td>—</td>
<td>14</td>
<td>[51, 49]</td>
</tr>
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</table>

Table 5. Comparison between formation enthalpies of alkali alanates and borohydrides from experiments and DFT calculations, respectively. Units are kJ/mol compound.
5 Summary

In this report a number of different ways of estimating the hydride formation enthalpy, $\Delta H_f$, of both binary and ternary hydrides have been reviewed: Born-Haber cycle, The Miedema model, Effective Medium Theory, The rule of reversed stability, and Density Functional Theory. Based on evaluation of model performance by comparison with experimental data (both for binary hydrides and ternary complex hydrides) the most versatile and accurate method is found to be Density Functional Theory.
References


In order for the hydrogen based society viz. a society in which hydrogen is the primary energy carrier to become realizable an efficient way of storing hydrogen is required. For this purpose metal hydrides are serious candidates. Metal hydrides are formed by chemical reaction between hydrogen and metal and for the stable hydrides this is associated with release of heat ($\Delta H_f$). The more thermodynamically stable the hydride, the larger $\Delta H_f$, and the higher temperature is needed in order to desorb hydrogen (reverse reaction) and vice versa. For practical application the temperature needed for desorption should not be too high i.e. $\Delta H_f$ should not be too large. If hydrogen desorption is to be possible below 100°C (which is the ultimate goal if hydrogen storage in metal hydrides should be used in conjunction with a PEM fuel cell), $\Delta H_f$ should not exceed -48 kJ/mol. Until recently only intermetallic metal hydrides with a storage capacity less than 2 wt.% H$_2$ have met this criterion. However, discovering reversible hydrogen storage in complex metal hydrides such as NaAlH$_4$ (5.5 wt. % reversible hydrogen capacity) have revealed a new group of potential candidates. However, still many combination of elements from the periodic table are yet to be explored. Since experimental determination of thermodynamic properties of the vast combinations of elements is tedious it may be advantageous to have a predictive tool for this task. In this report different ways of predicting $\Delta H_f$ for binary and ternary metal hydrides are reviewed. Main focus will be on how well these methods perform numerically i.e. how well experimental results are resembled by the model. The theoretical background of the different methods is only briefly reviewed.