A semi-empirical approach to accurate standard enthalpies of formation for solid hydrides

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Abstract
A semi-empirical method for estimation of enthalpies of formation of solid hydrides is proposed. The method is named \textit{Ionic} for short. By combining experimentally known enthalpies of formation for simple hydrides and reaction energies computed using band-structure density functional theory (DFT) methods, startling accurate results can be achieved. The approach relies on cancellation of errors when comparing DFT energies for systems with similar electronic structures. The influence of zero-point energies, polaritons, and vibrational excitations on the results has been examined and found to be minor.

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1. Introduction
Thermodynamic data are of fundamental importance for evaluation of the potential usefulness of a given complex hydride as a hydrogen storage medium. Adsorption and desorption reactions are often used to extract experimental values for standard enthalpy and entropy for complex hydrides through utilization of the van’t Hoff relation

\[
\frac{d(\ln K)}{dT} = \frac{\Delta H}{RT^2},
\]

where \( K \) is the equilibrium constant at temperatures \( T \), \( R \) is the ideal gas constant, and \( \Delta H \) is the enthalpy change of the reaction. However, although the natural logarithm of the equilibrium constant (which deduces the change in Gibbs free energy) can be determined by high accuracy, its derivative (viz. slope) with respect to temperature (which determines the partition of the Gibbs free energy into enthalpy and entropy contributions) may be less well defined. Moreover, for reasons of reaction kinetics, reaction-based studies frequently rely on measurements at high temperatures and pressures, which may necessitate extensive extrapolation. Alternatively, the partition of the Gibbs free energy into enthalpy and entropy can be accurately obtained from integrated heat capacities (e.g., standard-state quantities on integration of \( C_p \) over the range \( \sim 0 \) to 298 K). To the best of our knowledge, such high-quality data are rarely available for complex hydrides, and experimental values for enthalpy and/or entropy of formation must therefore be regarded with some circumspection [1].

Even though the individual absolute values for 0 K enthalpies derived through calculations based on density functional theory (DFT) are generally far from attaining the goal of chemical accuracy (\( \sim 5 \) kJ/mol), such data can still be used to estimate energetic differences involved in chemical reactions. The reason for this favorable feature is the highly consistent character of the errors made in the current DFT implementations, and reaction enthalpies derived in this way may accordingly be of considerable interest. DFT with plane-wave basis sets have previously been used to estimate formation enthalpies [1–5] for complex hydrides. For such uses, the limitations of contemporary density functionals must be well understood, enabling the practitioner to exploit cancellation of error to the greatest
extent possible. A prominent error present in most popular functionals is the so-called self-interaction error [6]. It particularly influences the reaction energies of redox reactions, in which electron density is transferred between different moieties of the molecular or crystalline system under study. DFT gives better estimates of reaction energies when the bonding characteristics of the reactants and products are similar. The situation is somewhat analogous to the concept of “isodesmic reactions” used in molecular quantum chemistry (reactions in which the number and type of bonds formed in the product(s) are the same as those broken in the reactant(s)). Reactions in which solid phases are compared to gaseous phases bring about several sources of error. First, the accuracy of the descriptions of the wavefunctions are bound to be different. Second, reactions generating or consuming gaseous molecules are usually redox reactions. The same is true for reactions which involve both metals and insulators: the bonding characteristics are fundamentally different, and electronic excitations will be significant in the metal(s), but not in the insulator(s).

The most important contributors to Gibbs free energy data assessed by DFT calculations for a chemical reaction are ground-state electronic energy, electron excitations, zero-point vibrations, and vibrational excitations. The importance of the zero point vibrational energy (ZPE) in such estimates for complex hydrides have been discussed by Ke et al. [3]. The significance of polaritons for the energetics of non-redox reactions between solids is likely to be minor.

The highest accuracy for reaction enthalpies calculated according to the DFT approach is, to our belief, obtained for cases where all reactants and products are wide-bandgap insulators. In such systems, electronic excitations can be ignored unless very high temperatures are considered. Further, the harmonic approximation used for phonon calculations are usually valid and one can normally reckon on reactions of the non-redox type. Reactions which involve wide-bandgap insulators only, are just the focus of this work where we aim at demonstrating a fast and reasonably accurate semi-empirical approach to the estimation of formation enthalpies.

In the following, we will present the validity of assuming a negligible difference in vibrational contributions to the standard enthalpy of formation between binary and multinary saline (and complex) hydrides. With this assumption in place the standard enthalpy of formation \( H_f^0 \) of saline solid \( A \) can be calculated from the standard enthalpy of formation \( \Delta H_f^0 \) of saline solids \( B \) through the Ionic scheme:

\[
\Delta H_f^0 A = \Delta H_f^0 B + \Delta E_f^{0K},
\]

where \( \Delta E_f^{0K} \) is the difference in electronic energy of the “reactant” \( A \) and “products” \( B \) calculated by DFT at 0 K. Notice that solids can be specified in negative quantities in \( B \). As an illustration one can calculate the enthalpy of formation of NaH through the artificially constructed reaction NaH \( \Rightarrow \) NaMgH\(_3\) – MgH\(_2\) from

\[
\Delta H_f^0 \text{NaH} = \Delta H_f^0 \text{NaMgH}_3 - \Delta H_f^0 \text{MgH}_2 + E_f^{0K} \text{NaH} - E_f^{0K} \text{NaMgH}_3 + E_f^{0K} \text{MgH}_2.
\]

2. Computational details

A somewhat intricate approach was used to calculate the phonon densities of states (phonon DOS). First the unit cells of all involved crystal structures were relaxed using band-structure calculations and the PAW scheme [7] as implemented in the VASP program package [8]. The optimizations were started from crystal structures reported in the ICSD database [9]. The only constraints on unit-cell parameters or fractional coordinates were those necessary to keep the symmetry unchanged. The Phonon program developed by Parlinski [10] was used for phonon calculations: the required supercell and force calculations were computed using the VASP code, and the resulting data were imported into the Phonon program. Thereafter the full Hessian was determined and the phonon DOS calculated. The Phonon and VASP programs were interfaced by means of locally developed software. The temperature dependence of the vibrational contributions to \( \Delta H \) and \( \Delta G \) were then calculated from the phonon DOS, again using locally developed software. Born effective charges were calculated utilizing the VASP package and Berry phase calculations via the King-Smith and Vanderbilt [11] method.

The density functional of Perdew et al. [12,13] was utilized for all calculations. Structure relaxation was performed with an energy cutoff of 500 eV, a force convergence criterion of 4 meV Å\(^{-1}\), and a Gaussian smearing with a standard deviation of 0.2 eV. Further, SCF convergence was considered achieved when the energy difference between two successive iterations was less than 10\(^{-7}\) eV. The \( k \) points for Brillouin zone integration were determined using a gamma-centered \( k \) mesh and a \( k \)-point density constant [14] of 15,000 \( k \)-points Å\(^3\). The force calculations used similar parameters, but with a \( k \)-point density of 1050 \( k \)-points atom [14].

The supercells used for (long-wavelength) phonon calculations were selected with the intention to cover a sphere with a diameter of 10 Å. A maximum constraint of about 140 atoms, however, restricted some cells to exhibit axis shorter than 10 Å, but no cell with an axis length below 7.5 Å has been used. The Hessian (harmonic approximation) was determined through numerical derivation using steps of 0.03 Å in both positive and negative directions of each coordinate to estimate the harmonic potentials. The sampling of the phonon band structure for the phonon DOS calculations were set to “large” in the Phonon program [10] with a point spacing of 0.05 THz. When polariton effects were included, these were approximated by a non-analytical semi-empirical term [15] as implemented in the Phonon program.

3. Results and discussion

To test the accuracy of thermodynamic functions derived on the basis of DFT calculations, the effects of polaritons, supercell size, and lattice expansion were examined. As mentioned, polaritons are not expected to affect the thermodynamic functions significantly, but affirmation of such a feature is still important. The temperature variation of \( \Delta G_{\text{vib.}} \) (i.e. \( \Delta H_{\text{vib.}} - T \Delta S_{\text{vib.}} \)) for MgH\(_2\) and KH was calculated with and without polariton effects.
Fig. 1. ∆G_{vib.+ZPE} (thick line), ∆H_{vib.+ZPE} (thin line), and −T∆S_{vib.} (difference between ∆G_{vib.+ZPE} and ∆H_{vib.+ZPE}) contributions of polarons for KH (a) and MgH2(b). Difference in zero point energy (ZPE), which is the sole contribution at zero temperature, can be seen to be the strongest effect.

On subtracting the latter from the former, it can be seen from Fig. 1 that there are indeed some changes in the ZPE, while the vibrational energy and entropy only change slightly. The actual contributions, which appear to be highest for systems of low symmetry, amount to less than 1 kJ/mol. Moreover, they can be expected to cancel in many of the reactions, as polariton effects are present in the products as well as the reactants. Our partial conclusion is accordingly that polariton effects can be neglected within the accuracy of the DFT approach.

The effect of thermal expansion of the lattice (which enters due to the perturbations of the phonon bands at higher temperatures) has been roughly estimated by considering the reaction NaH + MgH2 → NaMgH3 at 10% volume expansion. In these calculations, all structural parameters were allowed to relax freely under the sole constraints of increased cell volume and unchanged symmetry. Fig. 2 shows the difference in ∆G_{vib.} for the reaction with expanded lattices subtracted the corresponding findings for non-expanded lattices. As can be seen, the effects are virtually negligible, but we must emphasize that our model assumes equal thermal expansion for all phases involved, and hence the results must be considered as a rough estimate. However, the present findings display effects of thermal expansion that are of such a small magnitude that the approximation implied by calculating phonon band structures at 0 K rather than higher temperatures must be regarded as entirely valid.

The accuracy of the phonon contributions is highly dependent on the accuracy of the description of the phonon modes close to the gamma point. To calculate these correctly, long-range interactions must be taken into consideration. This was carried out by creating supercells of different sizes and estimating the Hessian matrix for long-range phonons. To test the convergence of this approximation, the thermodynamic functions for NaMgH3 was studied in a 2-2-2 supercell and compared to the corresponding findings for 2-1-2, 1-1-2, and 1-1-1 supercells. Fig. 3 shows that the convergence was far better than required for our purpose. In fact, even the original 1-1-1 cell might have been sufficient. Similar calculations were performed for Na3AlH6 for a 2-2-2 supercell and compared to the findings for 1-1-1, 1-2-1, and 2-2-1 supercells. At 300 K the resulting differences in ∆H_{vib.+ZPE} were 2.3, 1.6, and 0.8 kJ/mol, respectively, while the differences in ∆G_{vib.+ZPE} were −0.1, −0.4, and 0.5 kJ/mol. ∆H_{vib.+ZPE} at 300 K is in this case smaller than those of the vibrational energies due to imaginary frequencies in the 1-1-1, 1-2-1, and 2-2-1 cells. The imaginary contribution diminishes with the size of the unit cell, explaining the observed trend (the integral of the phonon DOS is thus larger for the larger cells). In any case, these results show that the convergence is likely to be on an acceptable level at a unit-cell size of 10^3 Å^3. This finding is very gratifying in view of the large extent to which systematic errors have been canceled out. Additionally, we note that the (already very small) errors arising from exclusion of long-wavelength phonons can be expected to cancel to some extent when computing reaction energies according to this approach.

Fig. 2. The dependence of the thermodynamic functions on lattice expansion for the net reaction NaH + MgH2 → NaMgH3. The thermodynamic functions for the reaction were evaluated for the systems at the a 10% volume expansion and subtracted the equivalent functions at the 0K equilibrium. ∆G_{vib.+ZPE} is represented by a thick line, ∆H_{vib.+ZPE} by a thin line, while −T∆S_{vib.} is the difference between ∆G_{vib.+ZPE} and ∆H_{vib.+ZPE}.
Fig. 3. Variation of vibrational thermodynamical quantities with supercell size and temperature. $\Delta G_{\text{vib}} + ZPE$ (thick line), $\Delta H_{\text{vib}} + ZPE$ (thin line), and $-T\Delta S_{\text{vib}}$ (difference between the thick and thin line). The graphs show (from top to bottom) the thermal functions of the 1-1-1, 1-1-2, and 2-1-2 supercell subtracted those of the 2-2-2 supercell. The effects on the thermal function can be seen to be small for the NaMgH$_3$ system.

To explore thermodynamic effects of phonons in non-redox reactions of hydrides, several reaction paths from binary to ternary hydrides were examined. Fig. 4 depicts a typical relation for thermodynamic functions vs. temperature for such reactions. This reaction exhibits a negative ZPE, and more important, the net vibrational enthalpy which counteract the change in ZPE. This behavior is typical for most of the reactions we have studied here and can be attributed to the fact that a comparatively high ZPE signifies fewer excited phonons.

The mechanisms behind these findings can be understood by recalling that a high ZPE signifies strongly bonded hydrogen atoms. The negatively charged hydrogen atoms in the hydrides under consideration may be viewed as a mediator, bonding cations to other cations. If the hydrogen atoms are strongly bonded, the indirect interactions between the cations will be determined by the hydrogen–cation bond. One way to view this is to visualize a one-dimensional chain of alternating cations and hydrogen anions in which the bonds are represented by springs. If the mass of the hydrogen anion in such a chain can be neglected compared to the mass of the cation, the effective spring constants between the cations will be proportional to that between cation and hydrogen. Consequently, a high relative ZPE reflects a strengthening of the interaction between heavy cations and thus moves the low energetic phonon branches to higher energy levels, which require higher temperatures for excitation. The thermodynamic effect of a high relative ZPE in a reaction is thus counteracted by an opposite trend in the vibrational enthalpy at moderate temperatures. Our general experience thus far is that, at 300 K, the effect of relative ZPE is larger than that of lowered relative number of phonon excitations, but in most cases they are of comparable magnitude. Table 1 lists the energy terms for a number of reactions from other hydrides. The trend of ZPE being counteracted by a lowered number of excitations is valid in most cases although there are exceptions (typically for reactions with small changes in ZPE).

The reactions from binary to ternary saline hydrides show negligible vibrational energy differences at 300 K, and in most of these cases, the mentioned mechanism of ZPE counteraction is noted. The consistent excellent agreement with experiment in these reactions is, as pointed out in Section I, due to the very similar bonding characteristics in the reactants and products of the reactions.

If one proceeds to examine reactions involving both complex hydrides, binary and ternary saline hydrides, and AlH$_3$, larger relative differences in ZPE and vibrational energy at 300 K are

Fig. 4. $\Delta G_{\text{vib}} + ZPE$ (thick line), $\Delta H_{\text{vib}} + ZPE$ (thin line), and $-T\Delta S_{\text{vib}}$ (difference between $\Delta G_{\text{vib}} + ZPE$ and $\Delta H_{\text{vib}} + ZPE$) for the net reaction NaH + MgH$_2$ → NaMgH$_3$. 

Table 1
Resulting net energies for a selected set of non-redox reactions which involve hydrides

<table>
<thead>
<tr>
<th>Reactants → Product</th>
<th>Energy term</th>
<th>Standard enthalpies of formation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta H_{ZPE}$</td>
<td>$\Delta H_{ZPE+vib.}$</td>
</tr>
<tr>
<td>Saline hydrides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaH + MgH$_2$ → NaMgH$_3$</td>
<td>−0.4</td>
<td>−0.2</td>
</tr>
<tr>
<td>KH + MgH$_2$ → KMgH$_3$</td>
<td>0.0</td>
<td>−0.8</td>
</tr>
<tr>
<td>2KH + MgH$_2$ → K$_2$MgH$_4$</td>
<td>0.9</td>
<td>−0.1</td>
</tr>
<tr>
<td>2RbH + MgH$_2$ → Rb$_2$MgH$_5$</td>
<td>−3.4</td>
<td>−0.8</td>
</tr>
<tr>
<td>3RbH + MgH$_2$ → Rb$_3$MgH$_6$</td>
<td>−3.0</td>
<td>−0.3</td>
</tr>
<tr>
<td>2CsH + MgH$_2$ → Cs$_2$MgH$_5$</td>
<td>−2.2</td>
<td>0.0</td>
</tr>
<tr>
<td>3CsH + MgH$_2$ → Cs$_3$MgH$_6$</td>
<td>−2.1</td>
<td>−0.1</td>
</tr>
<tr>
<td>KMgH$_3$ + KH → K$_2$MgH$_4$</td>
<td>0.9</td>
<td>0.7</td>
</tr>
<tr>
<td>Rb$_2$MgH$_5$ + RbH → Rb$_3$MgH$_6$</td>
<td>0.4</td>
<td>0.5</td>
</tr>
<tr>
<td>Cs$_2$MgH$_5$ + CsH → Cs$_3$MgH$_6$</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>CsH + CaH$_2$ → CsCaH$_3$</td>
<td>−2.0</td>
<td>−1.4</td>
</tr>
<tr>
<td>RbH + CaH$_2$ → RbCaH$_3$</td>
<td>−3.5</td>
<td>−1.6</td>
</tr>
<tr>
<td>Complex hydrides</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LiH + AlH$_3$ → LiAlH$_4$</td>
<td>−5.2</td>
<td>−1.5</td>
</tr>
<tr>
<td>NaH + AlH$_3$ → NaAlH$_4$</td>
<td>−1.9</td>
<td>0.2</td>
</tr>
<tr>
<td>KH + AlH$_3$ → KAlH$_4$</td>
<td>−3.8</td>
<td>−0.1</td>
</tr>
<tr>
<td>3LiH + AlH$_3$ → Li$_3$AlH$_6$</td>
<td>−0.4</td>
<td>1.4</td>
</tr>
<tr>
<td>3NaH + AlH$_3$ → Na$_3$AlH$_6$</td>
<td>2.4</td>
<td>3.0</td>
</tr>
<tr>
<td>CaH$_2$ + AlH$_3$ → CaAlH$_5$</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>CaH$_2$ + 2AlH$_3$ → Ca(AlH$_4$)$_2$</td>
<td>−9.3</td>
<td>−2.8</td>
</tr>
<tr>
<td>CaAlH$_3$ + AlH$_3$ → Ca(AlH$_4$)$_2$</td>
<td>−10.8</td>
<td>−4.6</td>
</tr>
<tr>
<td>2CaAlH$_3$ → CaH$_2$ + 3Ca(AlH$_4$)$_2$</td>
<td>−12.3</td>
<td>−6.3</td>
</tr>
<tr>
<td>LiAlH$_3$ + 2LiH → Li$_4$AlH$_8$</td>
<td>4.8</td>
<td>2.9</td>
</tr>
<tr>
<td>NaAlH$_4$ + 2NaH → Na$_3$AlH$_6$</td>
<td>4.2</td>
<td>2.8</td>
</tr>
</tbody>
</table>

All values are given in kJ/mol. Vibrational energies are given at 300 K and can be seen to be smaller than that of the zero point energy (ZPE) in most cases. The contribution of vibrational energy is negligible when compared to the electronic contribution or the overall enthalpy of formation. For calculation of standard enthalpies of formation the following corresponding binary hydride values were utilized (kJ/mol): LiH, −90.6 [16]; NaH, −56.4 [16]; KH, −57.8 [16]; RbH, −47.4 [16]; CsH, −49.9 [16]; MgH$_2$, −79.2 [16]; CaH$_2$, −181.5 [16]; AlH$_3$, −117.17 [17].

$^a$ Theoretically calculated from formation reactions and only including the difference in electronic energy [1].

$^b$ Theoretically calculated from formation reactions by including both changes in electronic and vibrational corrections [4].

$^c$ Derived by adding the experimental value for the reaction NaH + (1/3)Al + (1/2)H$_2$ → (1/3)Na$_3$AlH$_6$ to the enthalpy of formation for NaH.

noted. If the energies are measured per mol H$_2$, instead of per mol formula units, values are more comparable to the findings where only saline hydrides are involved, but still there is a notable increased discrepancy. We note that the only discrepancy as high as 3 kJ/mol refers to that of Na$_3$AlH$_6$ (Table 1, complex hydride reaction nr. five), which amounts to 19.9 kJ/mol compared to the findings of Bogdanovic et al. [19]. This result arouses suspicion regarding the experimental result, and indeed, there is evidence suggesting that the experimental value may be in error [23].

Most of the inconsistencies in Table 1 are likely due to a qualitative changes in bonding between the reactants and the products. First off, AlH$_3$ exhibits 3-center, 2-electron bonds, so-called banana bonds or hydrogen-bridge bonds. Such bonds are not present in any of the hydrides in Table 1 (except CaAlH$_5$ which exhibits chains of condensed AlH$_6$ octahedra), and in all likelihood this distinction in bonding character is, at least partly, able to account for the larger inconsistencies in the thermo-dynamic data for these reactions. Another important structural bonding feature is the different coordination of Al in LiAlH$_4$, NaAlH$_4$, KAlH$_4$, and Ca(AlH$_4$)$_2$ on the one hand and Li$_3$AlH$_6$, Na$_3$AlH$_6$, and CaAlH$_3$ on the other. The lower symmetry of the complex hydrides and the consequent appearing difference in number of optic bands might also have a certain effect. However, the boundary condition of zero-value derivative at the Brillouin zone boundary, bends the lower band down while the upper band is bent up. These two effects cancel to some degree from a thermodynamical point of view. All vibrational corrections to the enthalpy of formation are small and less than 1.5 kJ/mol H$_2$.

In conclusion, reaction enthalpies for reactions of the type considered in this report may be accurately estimated through the Ionic semi-empirical scheme. By using readily available experimental heats of formation for the simplest hydrides (or extremely accurate calculated values), we rely on cancellations of errors in the DFT description of the electronic structures to arrive at reliable results. Contributions from phonons are likely to cancel at 300 K, and the omission of such calculations allows great savings both in man-hours and computer time.

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