

The Thermodynamic Way of Assessing Reversible Metal Hydride Volume Expansion: Getting a Grip on Metal Hydride Formation Overpotential

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Abstract

The relative volume expansion of reversible metal hydride crystals upon formation is determined by means of the van't Hoff reaction entropy and STP ideal gas parameters, the development of this approach leads to a general method for calculating metal hydride single-crystal density. These results allow highlighting the pressure requirement to hydride phase formation, shown by the example of Ti-NaAlH₄.

1. Introduction

Reversible metal hydrides show upon hydrogenation a substantial volume change, e.g. up to about +40% for $V \rightarrow VH_2$,¹ which is an important safety aspect to consider in the design of metal hydride tanks. However, due to the powdery, transient nature of metal hydride beds, measurement of expansion forces is not trivial;² compaction into pellets is not a remedy since the additional compression energy put into the material makes its presence forcibly felt once the system runs through sorption cycles,^{3,4} hence it rather aggravates the issue. Calculations might offer a way out but do not represent simple undertakings for a powder bed of transient properties.^{5,6} Thus, it is reasonable to ask for a new method of practical simplicity: since hydrogen sorption reactions are reversible processes of a thermodynamic two-phase gas-sorbent system, it must be possible to gain the sought information from the van't Hoff parameters.

2. Methodical Approach

The problem is approached from a pV -energy balance point of view, comparing the metal and the metal hydride state of a system at IUPAC standard temperature and pressure (STP) because the van't Hoff parameters ΔH and ΔS of the hydrogenation reaction have an implicit reference to $p^\circ = 1$ bar. The hydrogenation process changes the density of the sorbent in the following manner: 1 g of metal assume a certain volume V (i.e. the density ρ); placing this gram-volume element in a hydrogen atmosphere at p° entails the formation of the metal hydride while the chemical potential of the gas phase changes by $-\Delta H = \mu_{H_2}$ and pressure above the sorbent drops to a fraction x of p° .⁷ In order to re-establish a pressure of p° above the sorbent, the temperature $\Delta H/\Delta S = T_{1\text{bar}}$ is required. While the initial hydrogenation pressure p° drops to a fraction x , the metal volume expands by ΔV and at the end of the absorption process, the chemical potentials of the gas and sorbent phase are on parity. Pressure is force per area and at thermodynamic equilibrium there must be force neutrality, thus the fraction x of p° is a measure for the relative volume expansion $\Delta V_\%$ of a gram-volume element of hydrogen sorbent. The above basic process description is shown in equation 1a; equation 1b expresses the same information by means of densities: index $_M$ refers to the initial metal or sub-hydride stage and index $_{MH}$ to the final hydrogenated state.

$$\rho_M = \frac{1 \text{ g}}{V_M} \xrightarrow[1 \text{ bar}]{H_2} \frac{1 \text{ g}}{p^\circ V_M} = \frac{1 \text{ g}}{x p^\circ V_{MH}} \Rightarrow x = \frac{V_M}{V_{MH}} = \Delta V_\% \quad (1a)$$

$$\frac{\rho_M}{p^\circ} = \frac{\rho_M - \rho_{MH}}{x p^\circ} \Rightarrow \frac{x p^\circ}{p^\circ} = x = 1 - \frac{\rho_{MH}}{\rho_M} = \Delta V_{\%} \quad (1b)$$

3. Results

Thus identifying the fraction x of p° at which the system settles in the hydrogenated state is a matter of the essence and making use of the ideal gas law towards that end is sensible. Advantageously simple in structure, it nonetheless offers a good approximation for hydrogen behaviour at typical metal hydride reaction conditions ($T > 300$ K, $p < 100$ bar). Since $-\Delta H$ is equal to the excursion of the gas phase chemical potential from μ° ,⁷ it figures by amount to a pV_m -energy term expressible via the ideal gas law which is shown in equation 2.

$$-\Delta H = \mu_{H_2} := |p V_m| = R T \quad (2)$$

Equation 3a displays an ideal gas law proportionality term which relates equation 2 to the STP state: the absorption reaction enthalpy $-\Delta H = \mu_{H_2} := |p V_m|$ causes an excursion of the standard pressure p° to a fraction $x p^\circ$. The temperature $T = T_{1bar} = \Delta H / \Delta S$ re-establishes a pressure of p° above the sorbent: hence the reaction enthalpies cancel out which leaves factor x a function of the reaction entropy ΔS ; via factor x the relative volume expansion $\Delta V_{\%}$ is introduced as shown in equation 3b.

$$\frac{|p V_m|}{V_m^\circ} = \frac{-\Delta H}{V_m^\circ} = x p^\circ \frac{T}{T^\circ} \quad | \quad \Delta H / \Delta S = T_{1bar} \quad (3a)$$

$$x p^\circ = \frac{-\Delta H}{V_m^\circ} \frac{T^\circ \Delta S}{\Delta H} = - \frac{T^\circ \Delta S}{V_m^\circ} \Rightarrow x = - \frac{T^\circ \Delta S}{p^\circ V_m^\circ} = \Delta V_{\%} \quad | \quad (\Delta S < 0) \quad (3b)$$

4. Discussion

Equation 3b expresses the volume work in the sorbent via the entropy change ΔS of the hydrogenation reaction which is evidently sensible. Magnesium hydride may serve for a first test; the van't Hoff reaction entropy value bases on a work of BOGDANOVIĆ *et al*,⁸ it is the arithmetic mean of the genuine data value and the references presented, nine in total. Densities note commonly in g per cm³, hence joule is expressed in bar cm³ (0.1 J = 1 bar cm³) and V_m° is given in cm³. Equation 4a shows the calculation based on crystal densities (equation 1b),^{9,10} equation 4b those based on thermodynamic data (equation 3b).

$$\Delta V_{\%} = 1 - \frac{\rho_{MgH_2}}{\rho_{Mg}} = 0.1657 \quad (4a)$$

$$\rho_{Mg} = 1.738 \text{ g cm}^{-3} \quad \rho_{MgH_2} = 1.45 \text{ g cm}^{-3}$$

$$x = - \frac{T^\circ \Delta S}{p^\circ V_m^\circ} = \Delta V_{\%} = 0.1644 \pm 0.008 \quad (4b)$$

$$T^\circ = 273.15 \text{ K} \quad V_m^\circ = 22711 \text{ cm}^3 \quad p^\circ = 1 \text{ bar}$$

$$\Delta S = -136.7 \pm 6.7 \text{ J (mol H}_2\text{)}^{-1} \text{ K}^{-1} = -13.67 \pm 0.67 \text{ bar cm}^3 \text{ (mol H}_2\text{)}^{-1} \text{ K}^{-1}$$

The results obtained for the plain values differ by 1 % which may be called a good agreement: It is however to consider that this calculation bases on crystal densities and with regard to practical powder bed volume expansion, an according adjustment for the packing density is due which is simple enough.¹¹ The investigation is repeated in kind for Ti-doped NaAlH₄ based on the data by BOGDANOVIĆ *et al*;¹² the reactions of the system are shown in equations 5a to 5c (for desorption are ΔH and $\Delta S > 0$).



Equation 6 shows the calculation for the relative volume change in Ti-NaAlH₄ according to equation 5a.

$$x = - \frac{T^\circ \Delta S}{p^\circ V_m^\circ} = \Delta V\% = 0.1467 \quad (6)$$

$$T^\circ = 273.15 \text{ K} \quad V_m^\circ = 22711 \text{ cm}^3 \quad p^\circ = 1 \text{ bar}$$

$$\Delta S = -122 \text{ J (mol H}_2\text{)}^{-1} \text{ K}^{-1} = -12.2 \text{ bar cm}^3 \text{ (mol H}_2\text{)}^{-1} \text{ K}^{-1}$$

This result of +14.7 % volume change upon hydrogenation is in concise agreement to the result of SANDROCK *et al* who measured for the dehydrogenation reaction –14.7 %.¹³ The mono-dispersed spherical packing factor of the metal hydride bed \star may be identified on basis of the relevant crystal densities,^{14–16} shown in equations 7a and 7b.

$$1 - \frac{\rho_{MH}}{\star \rho_M} = 0.1467 \quad (7a)$$

$$\rho_{MH} = \rho_{\text{NaAlH}_4} = 1.27 \text{ g cm}^{-3} \quad \rho_M = \frac{\rho_{\text{NaH}} + \rho_{\text{Al}}}{2} = \frac{1.396 + 2.702}{2} \text{ g cm}^{-3} = 2.049 \text{ g cm}^{-3}$$

$$\star = - \frac{\rho_{MH}}{(0.1467 - 1) \rho_M} = 0.726 \quad (7b)$$

Equation 7b shows the result for factor $\star = 0.726$, reasonably close to the densest regular packing of mono-dispersed spheres ($\star = 0.74$). Since related to the reaction enthalpy ΔS , this approach carries further towards a matter at the core of metal hydride hydrogen storage: the question of minimum temperature and pressure necessary for complete re-hydrogenation, a critical design threshold to any metal hydride tank. For example, in the Ti-NaAlH₄ system, [AlH₄]-formation requires are about 79 bar at 125 °C, a pressure substantially above the van't Hoff pressure of about 32 bar according to equation 5b data. These conditions are not particularly new, SANDROCK *et al* reported them already in 2002,¹⁷ yet that formation overpotential issue was never duly recognized in literature until the author clarified it's nature on basis of fundamental kinetic and thermodynamic reaction parameters.¹⁸ Thus, the problem is already solved with general significance by an approach from the system's gas phase end but the flipside effect must be recognizable in a particular sorbent as well, though in terms of molar volume than pressure and

temperature. Towards that end, equation 6 is transformed for p° and inserted into the van't Hoff equation with subsequent transformations as shown in equations 8a to 8d. Note the argumentative switch towards desorption because in this case all negative arithmetic signs show for ΔH and $\Delta S > 0$.

$$p^\circ = \frac{T^\circ \Delta S}{x V_m^\circ} \quad | \quad \Delta S = 12.2 \text{ bar cm}^3 (\text{mol H}_2)^{-1} \text{ K}^{-1} \quad (8a)$$

$$\ln\left(\frac{p_{\text{eq}}}{p^\circ}\right) = -\frac{\Delta H}{R T} + \frac{\Delta S}{R} \quad | \quad \Delta H \text{ and } \Delta S > 0 \quad (8b)$$

$$\ln\left(\frac{x V_m^\circ p_{\text{eq}}}{T^\circ \Delta S}\right) = -\frac{\Delta H}{R T} + \frac{\Delta S}{R} \quad (8c)$$

$$T \left(\Delta S - R \ln\left(\frac{x V_m^\circ p_{\text{eq}}}{T^\circ \Delta S}\right) \right) = \Delta H = |p V_m| \quad (8d)$$

Equation 8d reflects the equilibrium condition from which via a little detour the prerequisite for hydrogen *staying* in the sorbent (thus favouring hydride formation) can be derived: Hydrogen desorption occurs in the equilibrium system if the temperature-entropy gain $-T\Delta S$ in the gas phase ($\Delta S > 0$) exceeds the negative desorption (thus absorption) enthalpy, which is a measure for hydrogen fixation capability. Accordingly, equation 8d is rearranged for molar volume and the Ti-NaAlH₄ global reaction enthalpy $\Delta H = 4005 \text{ bar cm}^3 (\text{mol H}_2)^{-1}$ is inserted (equation 9).

$$-\frac{T}{p} \left(\Delta S - R \ln\left(\frac{x V_m^\circ p_{\text{eq}}}{T^\circ \Delta S}\right) \right) = -|V_m| > -\frac{4005}{p} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad (9)$$

The derivative of the chemical potential with reference to pressure equals molar volume. With this key intermediate in the derivation of the ideal gas chemical potential from Gibbs's fundamental equation, the conditional expression for non-desorption respective hydride phase stability is set up as shown in equation 10, amount dashes can be omitted because $d\mu/dp$ clarifies the arithmetic sign information.

$$\frac{T}{p} \left(\Delta S - R \ln\left(\frac{x V_m^\circ p_{\text{eq}}}{T^\circ \Delta S}\right) \right) = \frac{d\mu}{dp} = V_m < \frac{4005}{p} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad (10)$$

Equation 10 sketches qualitatively why the equilibrium pressure may not be sufficient for hydride formation: that is the case if the chemical potential of the gas phase is not sufficient for providing the pV_m -energy necessary for volume expansion vital to hydride formation and allowing the system to settle at the new equilibrium composition. A closer investigation of the Ti-NaAlH₄ example requires knowledge of the molar volumes respective single-crystal densities of NaAlH₄ and Na₃AlH₆: the former is known but the density of Na₃AlH₆ must be assessed by the entropy method as shown in equations 11a and 11b.

$$x_{\text{Na}_3\text{AlH}_6} = -\frac{T^\circ \Delta S}{p^\circ V_m^\circ} = \Delta V_\% = 0.1503 \quad (11a)$$

$$T^\circ = 273.15 \text{ K} \quad V_m^\circ = 22711 \text{ cm}^3 \quad p^\circ = 1 \text{ bar} \quad \Delta S = -125 \text{ J (mol H}_2 \text{ K)}^{-1} = -12.5 \text{ bar cm}^3 (\text{mol H}_2 \text{ K)}^{-1}$$

$$1 - \frac{\rho_{\text{Na3AlH6}}}{\star \rho_M} = 0.1503 \quad \Rightarrow \quad \frac{\rho_{\text{Na3AlH6}}}{\star} = (-1) (0.1503 - 1) \rho_M = 1.46 \text{ g cm}^{-3} \quad (11b)$$

$$\rho_M = \frac{3 \rho_{\text{NaH}} + \rho_{\text{Al}}}{4} = 1.723 \text{ g cm}^{-3}$$

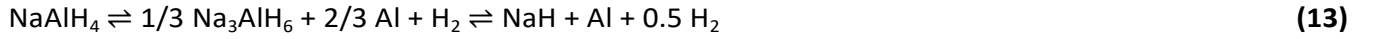
The respective molar volumes are now determined which is shown in equations 12a and 12b. Equation 12c displays the mean molar volume of the hydride phases in the global Na-Al-H reaction, given by the weighted geometric mean because of the transient nature of V_m in the equilibrium system.

$$M_{\text{NaAlH}_4} = 54 \text{ g mol}^{-1} \quad \rho_{\text{NaAlH}_4} = 1.27 \text{ g cm}^{-3} \quad \Rightarrow \quad V_{m,\text{NaAlH}_4} = 42.52 \text{ cm}^3 \text{ mol}^{-1} \approx 43 \text{ cm}^3 \text{ mol}^{-1} \quad (12a)$$

$$M_{\text{Na3AlH}_6} = 102 \text{ g mol}^{-1} \quad \rho_{\text{Na3AlH}_6} = 1.46 \text{ g cm}^{-3} \quad \Rightarrow \quad V_{m,\text{Na3AlH}_6} = 69.86 \text{ cm}^3 \text{ mol}^{-1} \approx 70 \text{ cm}^3 \text{ mol}^{-1} \quad (12b)$$

$$\bar{V}_{m,\text{Na-Al-H}} = \sqrt[3]{43 \cdot 43 \cdot 70 \text{ cm}^3 \text{ mol}^{-1}} = 50.58 \text{ cm}^3 \text{ mol}^{-1} \approx 51 \text{ cm}^3 \text{ mol}^{-1} \quad (12c)$$

For relating equation 12c to equation 10 respective the $[\text{AlH}_4]$ -formation issue, its transformation for the NaAlH_4 hydrogen equivalent molar volume Ψ_{m,NaAlH_4} is due as the reaction enthalpy ΔH refers to the mol hydrogen. Equation 13 shows how Ψ_{m,NaAlH_4} is obtained by multiplying the average molar volume with the stoichiometric proportion of the $[\text{AlH}_4]$ -stage in the total reaction, normalized to the NaAlH_4 equivalent.



$$\begin{aligned} \Psi_{m,\text{NaAlH}_4} &= \bar{V}_{m,\text{Na-Al-H}} \frac{1 \text{ mol Na-Al-H [for balance with } \bar{V}_{m,\text{Na-Al-H}}]}{2/3 \text{ mol NaAlH}_4 [\text{MH stoichiometric weight}]} \frac{1 \text{ mol NaAlH}_4 [\text{MH mol equivalent}]}{1.5 \text{ mol H}_2 [\text{total \# mol H}_2]} \\ &= 51 \text{ cm}^3 (\text{mol H}_2)^{-1} \end{aligned}$$

On basis of equation 13, the conditional pressure for $[\text{AlH}_4]$ -formation can be figured out as shown in equation 14a to 14c: the change in arithmetic sign due to the perspective switch from sorbent to gas phase between equations 14a and 14b is noteworthy,⁷ leading to the result that for $[\text{AlH}_4]$ -formation pressure needs to be larger than 78.53 bar \approx 79 bar.

$$\Psi_{m,\text{NaAlH}_4} < \frac{4005}{p} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad \text{sorbent phase} \quad | \quad -\Delta H = \mu_{\text{H}_2} \quad (14a)$$

$$p > \frac{4005}{\Psi_{m,\text{NaAlH}_4}} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad \text{gas phase} \quad (14b)$$

$$p > \frac{4005}{51 \text{ cm}^3 (\text{mol H}_2)^{-1}} \text{ bar cm}^3 (\text{mol H}_2)^{-1} = 78.53 \text{ bar} \approx 79 \text{ bar} \quad (14c)$$

The result of 78.5 bar in equation 14c for the minimum hydrogenation pressure is in excellent agreement with the old empiric value of about 79 bar,¹⁷ respective the result obtained from the gas phase-centred approach of 78.7 bar.¹⁸ It is noteworthy that approaching the issue from the gas phase perspective requires further knowledge of the activation energy but focussing on molar volume in the sorbent phase

encloses that information in blanket fashion: yet the gas phase approach offers more insight as yielding not only the threshold pressure but also the threshold temperature to hydride phase formation.¹⁸

A final point is made about why a pressure considerably above the $[\text{AlH}_4]$ -equilibrium pressure of 32 bar at 125 °C, e.g. 49 bar, results in the sole formation of Na_3AlH_6 : the fundamental prerequisite to $[\text{AlH}_4]$ -formation from the gas phase perspective is shown in equation 15a and equation 15b displays that a pressure of 49 bar leads to a conflict with it.

$$p > \frac{4005}{\bar{V}_{\text{m, NaAlH}_4}} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \Rightarrow \bar{V}_{\text{m, NaAlH}_4} = 51 \text{ cm}^3 (\text{mol H}_2)^{-1} > \frac{4005}{p} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad (15a)$$

$$\frac{4005}{49 \text{ bar}} \text{ bar cm}^3 (\text{mol H}_2)^{-1} = 81.7 \text{ cm}^3 (\text{mol H}_2)^{-1} \approx 82 \text{ cm}^3 (\text{mol H}_2)^{-1} \quad \nexists \quad (15b)$$

In turn, a calculation in kind of equation 13 for Na_3AlH_6 reveals the complementary reason why a hydrogenation pressure of 49 bar results solely in formation of Na_3AlH_6 , as shown in equation 16.

$$\bar{V}_{\text{m, Na}_3\text{AlH}_6} = \bar{V}_{\text{m, Na-Al-H}} \frac{1 \text{ mol Na-Al-H}}{1/3 \text{ mol Na}_3\text{AlH}_6} \frac{1 \text{ mol Na}_3\text{AlH}_6}{1.5 \text{ mol H}_2} = 102 \text{ cm}^3 (\text{mol H}_2)^{-1} \Rightarrow \Rightarrow p > 39 \text{ bar} \quad (16)$$

The realization that only the argumentative switch towards the gas phase allows the eventual conclusion of an issue which is allegedly entirely sorbent-phase related is a matter of essence. This refutes a narrow positivist understanding of the problem, emphasizing an exclusive sorbent phase bias of tangibles: declaring the essential non-essential breaches causality and must preclude convergence in outcome and insight alike. This work demonstrates that approaching a reversible metal hydride problem from either end of the equilibrium system leads to the selfsame result and thermodynamic principle(s) – that is as it should be – and underscores the expedient sensibility of determining sorbent-phase thermodynamic quantities by their ideal gas phase pendants (further bespoken by the van't Hoff equation). With regard to the threshold pressure to $[\text{AlH}_4]$ -formation, both approaches yield the same result, matching near-perfectly the empiric value of 79 bar.¹⁷

5. Conclusions

The relative volume expansion of a reversible metal hydride upon hydrogen absorption in terms of crystal densities can be determined from the van't Hoff reaction entropy and ideal gas IUPAC STP parameters. This ultimately allows insight into the prerequisites to metal hydride phase formation from a sorbent perspective which is the complementary specific flipside result of the general solution obtained if the issue of chemical overpotential to hydride formation is approached from a gas-phase vantage point.

6. Acknowledgements

This article originates from work done at FOTEC Forschungs- und Technologietransfer GmbH in Wiener Neustadt, Austria, under European Space Agency grant 4000105330/12/NL/CLP which is gratefully appreciated.

7. Conflicts of interest

There are no conflicts to declare.

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