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 change of reversible metal hydrides upon hydrogenation is determined by means of the van't Hoff reaction entropy and STP ideal gas parameters. This method allows insight into the requirements to metal hydride formation, outlined by example of Ti-NaAlH₄. This work presents a timeless perspective on the sorbent phase thermodynamics of reversible chemical hydrogen storage systems.

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, the powdery, transient nature of metal hydride beds makes the measurement of such expansion forces 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 hence it may even aggravate the issue.^{3,4} Calculations are a way out but these cannot be considered easy undertakings for a powder bed of transient properties.^{5,6} Thus, it is reasonable to ask for an alternate method of practical simplicity. Since the hydrogen sorption reactions are reversible processes of a thermodynamic two-phase gas-sorbent system, it must be possible to derive that information from the van't Hoff parameters.

2. Methodical Approach

The hydrogenation process is considered 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); the van't Hoff parameters ΔH and ΔS of the reaction have an implicit reference to $p^\circ = 1$ bar. The hydrogenation process changes thus the density of the sorbent: 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° results in 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 state and index $_{MH}$ to the final hydrogenated state.

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

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

3. Results

Thus, the matter breaks down to identifying the fraction x of p° at which the system settles in the hydrogenated state, approaching the issue via the ideal gas law 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; the van der Waals (vdW) equation yields a 6.8 % larger molar volume at 100 bar and 300 K). 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 as equation 2 shows.

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

Equations 3a and 3b show how relating equation 2 to the STP state by means of the ideal gas law yields the fraction x of p° ; the negative arithmetic sign in equation 3b is for formal reasons as ΔS and ΔH are both negative for the hydrogenation reaction.

$$\frac{|p V_m|}{V_m^\circ} = p^\circ \frac{T}{T^\circ} \quad | \quad \Delta H / \Delta S = T_{1bar} \quad -\Delta H = \mu_{H_2} = |p V_m| \quad (3a)$$

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

4. Discussion

Equation 3b expresses the volume work in the sorbent via the entropy change ΔS in the gas phase; for an ideal gas that makes evident sense. 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° given in cm³. Equation 4a shows the calculation based on material densities,^{9,10} equation 4b those by means of thermodynamic data respective 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.¹¹ The investigation may

be 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 the desorption reaction 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 $\ast$ may be identified on basis of the relevant crystal densities,^{14–16} as shown in equations 7a and 7b.

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

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

$$\ast = - \frac{\rho_{MH}}{(0.1467 - 1) \rho_M} = 0.726 \approx 0.73 \quad (7b)$$

Equation 7b shows the reasonable result for factor $\ast \approx 0.73$, close to the densest regular packing of mono-dispersed spheres ($\ast = 0.74$). Since related to the reaction enthalpy ΔS , this approach leads further to a matter at the core of metal hydride chemistry: the question of minimum temperature and pressure necessary for complete re-hydrogenation, a critical design threshold to any metal hydride tank. This shows e.g. in the Ti-NaAlH₄ system: for [AlH₄]-formation are about 79 bar at 125 °C required, a pressure is substantially above the equilibrium pressure of about 32 bar according to equation 5b. These conditions are not particularly new, SANDROCK *et al* reported them in 2002,¹⁷ yet that formation overpotential issue was never even recognized in literature until the author clarified it's nature on basis on fundamental kinetic and thermodynamic reaction parameters.¹⁸ Thus, the problem has been already solved with general significance by approaching it from the gas phase end but the flipside effect must be recognizable for a particular sorbent as well, though rather 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 (because ΔH and $\Delta S > 0$).

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

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

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

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

Equation 8d marks out the equilibrium condition; the prerequisite condition for hydrogen *staying* in the sorbent phase is outlined by inequality 9: in order to prevent desorption, the temperature-entropy gain $T\Delta S$ of the reaction ($\Delta S > 0$) must be for Ti-NaAlH₄ at least equal or smaller to the desorption enthalpy of $\Delta H = 4005 \text{ bar cm}^3 (\text{mol H}_2)^{-1}$ as by equation 5a,¹² the latter being by amount identical to the pV_m -energy change in the solid upon absorption.

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

The derivative of the chemical potential with reference to pressure equals molar volume, this key intermediate in the derivation of the ideal gas chemical potential from Gibbs's fundamental equation $dG = Vdp - SdT$ in relation to inequality 9 is shown in equation 10.

$$\frac{d\mu}{dp} = V_m \leq \frac{4005}{p} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad (10)$$

Equation 10 sketches the explanation for why a certain pressure above the equilibrium pressure can be a threshold to the hydrogenation reaction: 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* allow the system to settle at the new hydride equilibrium composition. A closer investigation of this requires thus knowledge of the molar volumes respective densities of NaAlH₄ and Na₃AlH₆. The former is available information; the density of Na₃AlH₆ must be assessed by the entropy method as in equations 11a to 11c.

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

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

$$1 - \frac{\rho_{MH}}{\star \rho_M} = 0.1503 \quad | \quad \star = 0.726 \quad (11b)$$

$$\rho_M = \frac{\rho_{\text{NaH}} + \rho_{\text{Al}}}{2} = 2.049 \text{ g cm}^{-3}$$

$$\rho_{\text{Na}_3\text{AlH}_6} = (-1) (0.1503 - 1) \star \rho_M = 1.26 \text{ g cm}^{-3} \quad (11c)$$

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

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

$$M_{\text{Na}_3\text{AlH}_6} = 102 \text{ g mol}^{-1} \quad \rho_{\text{Na}_3\text{AlH}_6} = 1.26 \text{ g cm}^{-3} \quad \Rightarrow \quad V_{\text{m,Na}_3\text{AlH}_6} = 80.95 \text{ cm}^3 \text{ mol}^{-1} \quad (12b)$$

$$\bar{V}_{\text{m,Na-Al-H}} = \sqrt[3]{42.52 \cdot 42.52 \cdot 80.95} \text{ cm}^3 \text{ mol}^{-1} = 52.70 \text{ cm}^3 \text{ mol}^{-1} \quad (12c)$$

Since the chemical potentials of the gas and the sorbent phase are mirror-wise coupled in an equilibrium system, any gain in chemical potential in the sorbent phase is equal to the loss of it in the gas phase: by amount, both must be equal by hydrogen equivalent as shown in equation 13.

$$\mu_{\text{H}_2} = \mu_{\text{MH}} \quad \Rightarrow \quad |V_{\text{m,H}_2}| = |V_{\text{m,MH}}| \frac{n_{\text{MH}}}{n_{\text{H}_2}} \quad (13)$$

The adjustment of equation 10 to equation 13 is displayed in equation 14 which a) shows the global equilibrium reaction equation expressed for one mol of NaAlH_4 with b) $\bar{V}_{\text{m,Na-Al-H}}$ as the weighted mean molar volume of the Na-Al-H phases according to their stoichiometric proportion in the total reaction but it is c) calibrated further for obtaining the *effective NaAlH₄ hydrogen equivalent molar volume* $\bar{V}_{\text{m,NaAlH}_4}$.

$$\begin{aligned} \bar{V}_{\text{m,NaAlH}_4} &= \bar{V}_{\text{m,Na-Al-H}} \frac{1 \text{ mol Na-Al-H [for balance with } \bar{V}_{\text{m,Na-Al-H}}]}{2/3 \text{ mol NaAlH}_4 \text{ [MH stoichiometric weight]}} \frac{1 \text{ mol NaAlH}_4 \text{ [MH mol equivalent]}}{1.5 \text{ mol H}_2 \text{ [total \# mol H}_2]} \\ &= 52.7 \text{ cm}^3 (\text{mol H}_2)^{-1} \end{aligned}$$

On basis of equation 14 it is possible to sort out the conditional pressure for $[\text{AlH}_4]$ -formation as shown in equations 15a to 15c, leading to the result of 76 bar.

$$\bar{V}_{\text{m,NaAlH}_4} \leq \frac{4005}{p} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad \text{sorbent phase} \quad | \quad \Delta H = -\mu_{\text{H}_2} \quad (15a)$$

$$p_{\text{H}_2} \geq \frac{4005}{\bar{V}_{\text{m,NaAlH}_4}} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad \text{gas phase} \quad (15b)$$

$$p_{\text{H}_2} \geq \frac{4005}{52.7 \text{ cm}^3 (\text{mol H}_2)^{-1}} \text{ bar cm}^3 (\text{mol H}_2)^{-1} = 76.0 \text{ bar} \quad (15c)$$

The result of 76 bar in equation 15c for the minimum hydrogenation pressure is in good 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 considering the multitude of steps necessary along the way. A final point may be made why a pressure considerably above the $[\text{AlH}_4]$ -equilibrium pressure of 32 bar at 125 °C like e.g. 49 bar may still result in formation of Na_3AlH_6 : equation 16a and 16b show that a pressure of 49 bar leads to a conflict with the fundamental $[\text{AlH}_4]$ -formation requirement of equation 15b.

$$\text{Requirement for } [\text{AlH}_4]\text{-formation: } 52.7 \text{ cm}^3 (\text{mol H}_2)^{-1} \geq \frac{4005}{p} \text{ bar cm}^3 (\text{mol H}_2)^{-1} \quad (16a)$$

$$\frac{4005}{49 \text{ bar}} \text{ bar cm}^3 (\text{mol H}_2)^{-1} = 81.7 \text{ cm}^3 (\text{mol H}_2)^{-1} \quad \nlessgtr \quad (16b)$$

The molar hydrogen volume in equation 16a represents the $d\mu/dp$ prerequisite to chemical potential of the gas phase for adopting the $[\text{AlH}_4]$ -equilibrium composition in the sorbent. However, a hydrogenation pressure of 49 bar does not suffice that criterion for allowing the system to settle at the new equilibrium composition. The calculation in kind for Na_3AlH_6 is shown in equation 17.

$$V_{\text{m},\text{Na}_3\text{AlH}_6} = \bar{V}_{\text{m},\text{Na-Al-H}} \frac{1 \text{ mol Na-Al-H}}{1/3 \text{ mol Na}_3\text{AlH}_6} \frac{1 \text{ mol Na}_3\text{AlH}_6}{1.5 \text{ mol H}_2} = 105.40 \text{ cm}^3 (\text{mol H}_2)^{-1} \Rightarrow \Rightarrow p_{\text{H}_2} \geq 38.0 \text{ bar} \quad (17)$$

This is the complementary result to equation 16b and explains why a hydrogenation pressure of 49 bar results only in formation of Na_3AlH_6 . It is noteworthy that only the argumentative switch towards the gas phase allows concluding the issue eventually, while keeping focus on the sorbent phase cannot lead towards convergence in insight. This work demonstrates that approaching a reversible metal hydride problem from either end of the equilibrium system may lead to the base thermodynamic principle, eventually. However, since determining sorbent-phase thermodynamic quantities by its ideal gas phase pendant is such a fundamental principle (bespoke by the van't Hoff equation) for convergence, the gas phase vantage point is preferable, especially if a general solution is desired. For the present example of conditional $[\text{AlH}_4]$ -formation pressure, the results by the two respective approaches are with 76 bar and 78.7 bar quite close to each other, they differ on average by just 3.5%. This is remarkable considering the ideal gas nature of the approach and that the results base on data from well-done yet different works. Considering further the manifold factors slightly affecting kinetic and thermodynamic metal hydride reaction data such as e.g. average particle size, it appears not sensible to emphasize the difference.

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 STP parameters. This ultimately offers insight about the prerequisites to metal hydride phase formation from a material perspective, although that particular issue can be more straightforwardly and completely resolved from the system's gas-phase end.

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7. Conflicts of interest

There are no conflicts to declare.

8. Notes and references

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