

On the Common Ground of Thermodynamics and Kinetics: How to Pin Down Overpotential to Reversible Metal Hydride Formation and the Complete Ideal Gas Theory of Reversible Chemical Hydrogen Storage

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Abstract

Ti-doped NaAlH₄ requires at 125 °C for [AlH₄] formation more than twice the equilibrium pressure; while it is straightforward to relate this conditional surplus in hydrogenation pressure respective chemical potential to kinetic hindrance, it appears strange that this matter has not been duly theoretically addressed in literature to this day. The interest in identifying such overpotentials is not of purely academic interest but touches a problem of practical significance as the maximum applied (i.e. hydrogenation) pressure is an important threshold to metal hydride tank design. A theory-based tool would be a resource-efficient complement or even alternative to PCI measurements. This paper tracks the formation overpotential issue down to its root and outlines a simple yet accurate general method based on Arrhenius and van't Hoff data. Rather unexpectedly, the result is also the final missing piece towards a comprehensive understanding of reversible chemical hydrogen storage with regard to attainable hydrogen storage capacity.

1. Introduction

It is one of the peculiarities of metal hydride chemistry that in the partially reversible Ti-doped NaAlH₄ system [AlH₄] formation requires a hydrogenation pressure substantially above the equilibrium pressure:^{1–3} e.g. about 80 bar at 125 °C versus an equilibrium pressure of about 29 bar.⁴

This surplus pressure suggests a sizeable kinetic barrier as the equilibrium pressure p_{eq} would be the marker hydrogenation pressure without kinetic hindrance. Considering the fundamental nature of reversible chemical hydrogen storage – essentially classic ideal gas equilibrium thermodynamics – it is a bit puzzling that no general theoretical method for assessing such a chemical overpotential seems to exist in literature. With regard to practical application, the maximum applied hydrogen pressure is the foremost quantity to metal hydride tank design and a simple theory-based tool for identifying overpotential pressure would undoubtedly prove of value to the art.

The problem is that neither the classic kinetic and thermodynamic metal hydride analysis tools – the Arrhenius equation and the van't Hoff equation – point a way how to get a grip on overpotential. Yet they simply must contain this piece of information which actually indicates a blind spot in the hitherto understanding of reversible chemical hydrogen storage in particular and physical chemistry in general. It is of course possible to determine the overpressure experimentally by a pressure-composition-isotherm (PCI) measurement: apart from that being a time-consuming matter requiring special equipment, this merely displaces the issue to the question which temperature to choose. While PCIs are a tool of value, they cannot be considered a substitute for a fundamental theoretical answer; hence it is worthwhile and necessary to investigate the nature of chemical overpotential in reversible systems. It is a matter of wider concern as touching the foundations of physical chemistry.

This paper outlines the method for determining the hydrogenation overpotential for any reversible chemical hydrogen sorbent by sole means of thermodynamic and kinetic reaction analysis data.

2. Methodical Approach

A higher conditional pressure to reversibility suggests a chemical overpotential with regard to the equilibrium pressure: for that reason it is sensible to start developing from the van't Hoff equation. For metal hydrides, the van't Hoff equation links the hydrogen equilibrium pressure above the sorbent to the thermodynamic reaction data ΔH_m° and ΔS_m° , reflecting reference to the mol hydrogen but using ΔH and ΔS without indexes is common in relevant literature. ΔH_m° and ΔS_m° are obtained from an extrapolation of $\ln(p_{eq}/p^\circ)$ versus $1/T$ towards standard pressure of $p^\circ = 1$ bar, thus the quotient $\Delta H_m^\circ/\Delta S_m^\circ$ yields the temperature for 1 bar equilibrium pressure above the sorbent, it is a material-specific constant. Equation 1 shows the van't Hoff relation for desorption.

$$\ln\left(\frac{p_{eq}}{p^\circ}\right) = -\frac{\Delta H_m^\circ}{R T} + \frac{\Delta S_m^\circ}{R} \quad | \text{ for desorption } \Delta H_m^\circ \text{ and } \Delta S_m^\circ > 0 \quad (1)$$

Why is equation 1 formulated for desorption if scope rests on the overpotential to metal hydride formation respective the absorption reaction? This may seem counterintuitive but reversibility in the thermodynamic sense is an ideal entity in which two different reaction pathways back and forth do not make sense. That in practice two seemingly different reaction pathways are observed does not unhinge the ideal base conception but is rather owed to the arithmetic sign requirements to ΔH_m° and ΔS_m° with regard to reversibility: the $+p\Delta V$ energy consumed by the volume expansion upon hydrogen absorption ($\Delta H_m^\circ < 0$) suffices for an asymmetry which splits the single reaction pathway into two. Equation 4 schematically illustrates the energy balance of a reversible metal hydride.

$$\Delta H_{m, abs}^\circ - (E_{a, abs} + p\Delta V) = -(\Delta H_{m, des}^\circ + E_{a, des}) \quad | \Delta H_{m, abs}^\circ < 0 < \{\Delta H_{m, des}^\circ; E_{a, des}; E_{a, abs}; p\Delta V\} \quad (4)$$

If in equation 4 the reaction enthalpies $\Delta H_{m, abs}^\circ(-)$ and $\Delta H_{m, des}^\circ(+)$ are exchanged by the arithmetic mean in terms of amount $\pm\Delta H_m^\circ$, the enthalpies cancel out and leave all quantities not visible to the van't Hoff analysis at parity as by equation 5, demonstrating the fundamental viability of the line of argument. Equation 5 respective its generalization enables an indirect approach starting from the desorption end of the system for capturing the essence of hydrogenation overpotential at the absorption end. That is because the system is a) reversible and b) it is only for desorption where the arithmetic sign convention makes for an expedient match: ΔH_m° , ΔS_m° and $E_{a, des}$ are all positive.

$$\begin{aligned} -\left(\frac{\Delta H_{m, abs}^\circ + \Delta H_{m, des}^\circ}{2}\right) - (E_{a, abs} + p\Delta V) &= -\left(\left(\frac{\Delta H_{m, abs}^\circ + \Delta H_{m, des}^\circ}{2}\right) + E_{a, des}\right) \Rightarrow \\ - (E_{a, abs} + p\Delta V) &= -E_{a, des} \end{aligned} \quad (5)$$

The following question conveys the essence of the indirect approach: *In a reversible metal hydride system, what chemical potential respective pressure is necessary to stop desorption cold at the apex of the activation energy?*

Figure 1 illustrates the hydrogen desorption from a reversible generic metal hydride MH_2 in an energy vs. reaction-coordinate scheme, all due quantities have a reference to the mol hydrogen.

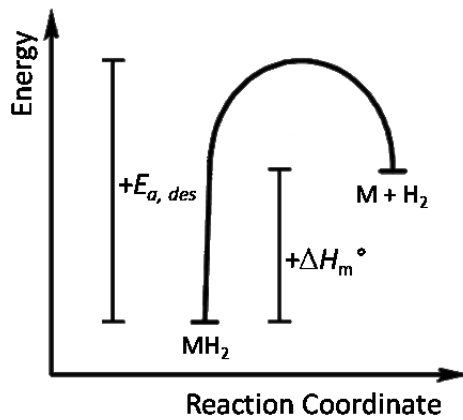


Figure 1: Energy vs. reaction-coordinate scheme for hydrogen desorption from a generic reversible metal hydride MH_2 .

For a reversible system without activation, changing the equilibrium system from metal hydride into the desorbed state requires the reaction enthalpy $+\Delta H_m^\circ$ being compensated by the temperature-entropy gain in the gas phase $-T\Delta S_m^\circ$; this is possible up to the equilibrium pressure p_{eq} . Figure 1 shows that the material proportion of the system moves energetically uphill in the desorption process which requires overcoming the activation energy barrier $E_{a, des}$. However, as desorption activation energy $E_{a, des}$ encompasses the reaction enthalpy $+\Delta H_m^\circ$, the overpotential E^* that must be additionally compensated by the temperature-entropy gain $-T\Delta S_m^\circ$ is given by $E^* = E_{a, des} - \Delta H_m^\circ$ which is shown in equation 6.

$$E_{a, des} - \Delta H_m^\circ = E^* \Rightarrow E^* - T\Delta S_m^\circ = 0 \quad | \{E_{a, des}; \Delta H_m^\circ; \Delta S_m^\circ > 0\} \quad (6)$$

The overpotential E^* in equation 6 stands in two relations to the van't Hoff parameters: *first*, division by ΔS_m° yields T^* which is the temperature rendering desorption versus 1 bar pressure viable. *Second*, division of E^* by the material constant $\Delta H_m^\circ/\Delta S_m^\circ = T_{1bar}$ yields the hypothetical entropy gain $\Delta S_m^{*\circ}$ which would be required for the activated system adopting an equilibrium pressure of 1 bar at the metal hydride specific temperature T_{1bar} . This is shown in equations 7a and 7b, respectively.

$$\frac{E^*}{\Delta S_m^\circ} = T^* \quad (7a)$$

$$\frac{E^*}{T_{1bar}} = \Delta S_m^{*\circ} \quad (7b)$$

Setting the van't Hoff equation up for $T = T^*$ with $\Delta S_m^{*\circ}$ in lieu of ΔS_m° yields the sought expression for the marker equilibrium hydrogen pressure p^* caused by overpotential, as shown in equation 8.

$$\ln \left(\frac{p^*}{p^\circ} \right) = -\frac{\Delta H_m^\circ}{R T^*} + \frac{\Delta S_m^{\circ*}}{R} \quad | \{ \Delta H_m^\circ; \Delta S_m^{\circ*} > 0 \} \quad (8)$$

This can be made more apparent if equation 8 is transformed into the form which equals the chemical potential of the gas phase with the 2nd law of thermodynamics, shown in equation 9.

$$R T^* \ln \left(\frac{p^*}{p^\circ} \right) = -\Delta H_m^\circ + T^* \Delta S_m^{\circ*} \quad | \{ \Delta H_m^\circ; \Delta S_m^{\circ*} > 0 \} \quad (9)$$

Division of equation 9 by ΔH_m° turns the $\Delta S_m^{\circ*}$ entropy term into a temperature proportionality term (equal by the ideal gas law to a quotient of pV_m -energies). This is shown in equations 10a and 10b.

$$\frac{R T^*}{\Delta H_m^\circ} \ln \left(\frac{p^*}{p^\circ} \right) = -1 + \frac{T^* \Delta S_m^{\circ*}}{\Delta H_m^\circ} = -1 + \frac{T^*}{T_{1\text{bar}}} \left(\frac{E_{a,\text{des}}}{\Delta H_m^\circ} - 1 \right) \quad (10a)$$

$$\frac{\Delta S_m^{\circ*}}{\Delta H_m^\circ} = \frac{E^*}{T_{1\text{bar}} \Delta H_m^\circ} = \frac{1}{T_{1\text{bar}}} \left(\frac{E_{a,\text{des}} - \Delta H_m^\circ}{\Delta H_m^\circ} \right) = \frac{1}{T_{1\text{bar}}} \left(\frac{E_{a,\text{des}}}{\Delta H_m^\circ} - 1 \right)$$

$$R T^* \ln \left(\frac{p^*}{p^\circ} \right) = \left(\frac{T^*}{T_{1\text{bar}}} \left(\frac{E_{a,\text{des}}}{\Delta H_m^\circ} - 1 \right) - 1 \right) \Delta H_m^\circ = \left(\frac{T^*}{T_{1\text{bar}}} \left(\frac{E_{a,\text{des}}}{\Delta H_m^\circ} - 1 \right) \right) \Delta H_m^\circ - \Delta H_m^\circ \quad (10b)$$

The left side of equation 10b is the chemical potential of the gas phase at temperature T^* at which the temperature-entropy gain in the system $-T^* \Delta S_m^\circ$ caused by hydrogen desorption suffices for compensating the kinetic barrier to the equilibrium system. The right side is an expression of energy differences illustrated in figure 1 but expressed in terms of ΔH_m° . The term $(E_{a,\text{des}}/\Delta H_m^\circ - 1)$ expresses the activation energy $E_{a,\text{des}}$ in multiples of ΔH_m° and subtracts the one ΔH_m° which is accounted for by the equilibrium system. That factor is multiplied with a quotient of the fix temperatures $T^*/T_{1\text{bar}}$ for reflecting the ratio of $E^*/\Delta H_m^\circ$. From equation 10b, the argumentative tacking from desorption towards absorption requires the realization that the summand $-\Delta H_m^\circ$ on the right side if $\Delta H_m^\circ > 0$ is equivalent to the addition of the negative absorption reaction enthalpy. For this reason, equation 11 shows the definite ideal gas expression for the marker equilibrium pressure p^* caused by chemical overpotential on basis of Arrhenius and van't Hoff analysis data.

$$\ln \left(\frac{p^*}{p^\circ} \right) = \left(\frac{T^*}{T_{1\text{bar}}} \left(\frac{E_{a,\text{des}}}{\Delta H_m^\circ} - 1 \right) - 1 \right) \frac{\Delta H_m^\circ}{R T^*} \quad | \{ \Delta H_m^\circ; \Delta S_m^\circ > 0 \} \quad (11)$$

$$T^* = \frac{E_{a,\text{des}} - \Delta H_m^\circ}{\Delta S_m^\circ} \quad T_{1\text{bar}} = \frac{\Delta H_m^\circ}{\Delta S_m^\circ}$$

3. Results

It is consequential to apply equation 11 to the overpotential issue encountered in the Ti-NaAlH₄ system. The Arrhenius activation energy values for [AlH₄] formation depend on Ti-concentration and range from 72.8 kJ (mol H₂)⁻¹ for 0.9 mol % Ti-doped NaAlH₄ to 80 kJ (mol H₂)⁻¹ for 4 mol % Ti-doped NaAlH₄ as by SANDROCK *et al.*⁴ The van't Hoff reaction parameters base on the data of BOGDANOVIĆ *et al* for 1.3 mol% Ti-doped NaAlH₄.¹ The 4 mol % Ti-case will be considered for an example:

$$\ln\left(\frac{p^*}{p^\circ}\right) = \left(\frac{T^*}{T_{1\text{bar}}}\left(\frac{E_{a,\text{des}}}{\Delta H_m^\circ} - 1\right) - 1\right) \frac{\Delta H_m^\circ}{R T^*} \quad | \quad T^* = \frac{E_{a,\text{des}} - \Delta H_m^\circ}{\Delta S_m^\circ} \quad T_{1\text{bar}} = \frac{\Delta H_m^\circ}{\Delta S_m^\circ}$$

$$\begin{array}{lll} \Delta H_m^\circ = +37 \text{ kJ (mol H}_2\text{)}^{-1} & \Delta S_m^\circ = +121 \text{ J (mol H}_2\text{)}^{-1} \text{ K}^{-1} & E_{a,\text{des}} = 80 \text{ kJ (mol H}_2\text{)}^{-1} \\ T_{1\text{bar}} = 306 \text{ K} & T^* = 355 \text{ K} & \Rightarrow \ln(p^*/p^\circ) = 4.365(6) \Rightarrow p^* = 78.7 \text{ bar} \approx 79 \text{ bar} \end{array}$$

4. Discussion

This result for a marker pressure of $p^* = 79 \text{ bar}$ for [AlH₄] formation complies perfectly with the reported minimum hydrogenation pressure of 79.5 bar by SANDROCK *et al* whose activation energy value is used,⁴ although SANDROCK *et al* do not mention this as result of an optimization effort. Yet it is unlikely that such an important experimental quantity would be left to chance at Sandia National Laboratory. The value of $T^* = 355 \text{ K}$ or 82°C is also in fine agreement with the empiric yet somewhat unspecific observation that desorption from Ti-NaAlH₄ materials becomes noticeable above ca. 80°C . The reason for that and how that temperature can be generally calculated from the kinetic and thermodynamic analysis data is now clear. Ti-concentrations below 1 mol % show considerably lower activation energies but the benefit is offset by the lower catalyst concentration; hence the potentially relevant Ti-concentrations are likely between 2 – 4 mol % for which near-identical activation energies are reported: $79.5 \text{ kJ (mol H}_2\text{)}^{-1}$ and $80 \text{ kJ (mol H}_2\text{)}^{-1}$, respectively.⁴ Equation 11 works of course only as well as the kinetic and thermodynamic data allow and already a deviation of a few kJ (mol H₂)⁻¹ in activation energy $E_{a,\text{des}}$ will result in an exponential error to the overpotential pressure p^* . However, the approach allows retro-checking for consistency, also with regard to experiment. In the present case the kinetic and thermodynamic data by Sandia National Laboratory and MPI für Kohlenforschung seem to match as indicated by a common $T_{1\text{bar}}$ temperature of 306 K .⁵

Thermodynamics and kinetics are commonly taught as separate entities: thermodynamics tells whether a reaction is possible, kinetics tells about the speed of possible reactions. Overpotential is thus usually understood as a kinetic issue because the activation energy is determined by kinetic analysis. However, it shows for reversible reactions that treating kinetic hindrance as integral part of the thermodynamic equilibrium system brings about a new quality in insight: then the overpotential E^* actually emerges as the kinetic hydrogen retention potential of a metal hydride, a silent reserve to the ΔH_m° equilibrium capacity. This is a comparatively active interpretation of the role the activation energy which is usually considered a passive obstacle to be dismantled for higher reaction rates. This realization sorts out every hitherto unclear principal aspect of reversible chemical hydrogen storage: e.g. it clarifies the nature of high activation, high hydrogen content but comparatively low reaction enthalpy hydrides, e.g. borohydrides.⁶ From the common fragmented understanding of thermodynamics and kinetics, these systems must appear by principle fully reversible with an

appealingly low $T_{1\text{bar}}$ temperature, so virtually all that would be needed for a marvellous energy storage density is getting rid of the activation barrier. Yet in light of the present work rather the opposite appears to be true, these low ΔH_m° materials are of high hydrogen content because of their high activation energy and removal of that barrier may render the system reversible but within the comparatively modest thermodynamic limits to equilibrium mass transfer previously outlined.⁷

However, it also shows now that an all-equilibrium perspective does not capture the full picture either. The disruptive surplus-to-equilibrium hydrogen amounts, resulting from co-doping in the K/Ti-co-doped- NaAlH_4 system,⁸ respective the Rb/K-co-doped $2\text{LiH}/\text{Mg}(\text{NH}_2)_2$ system,⁹ can be mostly explained on basis of intrinsic thermodynamic limitation to ideal gas equilibrium mass transfer.⁷ Although successful in clarifying the relation of equilibrium mass transfer to (partial) reversibility and providing a principal idea about the way such a surplus-to-equilibrium hydrogen amount gets into the sorbent phase, this equilibrium approach leaves the final question open, *how* that surplus is permanently retained there. It cannot be on grounds of equilibrium reaction enthalpy as the co-doping process leaves the thermodynamic reaction parameters of the base system virtually unscathed; actually it renders the enthalpy of desorption a bit smaller though that is explainable by the equilibrium approach as well. In contrast, the surplus-to-equilibrium hydrogen amount resulting from K-co-doping of Ti- NaAlH_4 figures to +42 % with regard to the base system! This work shows the only way how substantially more hydrogen capacity at somewhat less desorption enthalpy can be rationally explained: The surplus hydrogen amount is brought into the system in equilibrium manner but it is kinetically retained by means of the activation energy of the equilibrium system. That this was not realized before might be owed to the educationally instilled rift between thermodynamics and kinetics, pre-shaping thought. A possible lesson from that might be a revision of how this is taught in curriculums: showing the convergence of thermodynamics and kinetics in reversible systems is equally important to teaching their functional separation for irreversible ones. The vested interest in reversible chemical hydrogen storage may be subject to fancies but proper fundamental ideas never get outdated.

5. Conclusion

The relation between a thermodynamic two-phase gas-sorbent equilibrium system and its kinetic hindrance respective chemical overpotential is fundamental for a global and comprehensive understanding of reversible chemical hydrogen storage. Its clarification makes everything fall into place: the ideal limits to equilibrium mass transfer yield the definite boundaries to reversible hydrogen storage capacity; however, it may be possible to dope an equilibrium system for a metal hydride of a more negative formation enthalpy. This new reaction pathway connects to the base system in equilibrium manner and provides additional potential for hydrogen fixation from the gas phase (though not its permanent retention). This allows exceeding the equilibrium hydrogen amount in proportion to the additional enthalpy and the stoichiometric weight of the affected reaction(s) in the base equilibrium system. Kinetic hindrance is instrumental for permanently retaining such a surplus-to-equilibrium hydrogen amount in the sorbent. However, because this gain in hydrogen capacity results from essentially an equilibrium process still, it is by principle subject to the selfsame mass transfer limitations taking effect on the base equilibrium system. A metal hydride at the end of its equilibrium and kinetic hydrogen retention potential may be rendered capable of absorbing even more hydrogen by a combination of chemical kinetic stabilization and suitable pathway doping; however this may be seen rather an instructive hypothetical extreme of the principle at work than a practical notion. While identified for metal hydride hydrogen storage, the principle of intrinsic thermodynamic mass transfer limitation must be in adjusted form of significance to other reversible chemical systems, with special regard to electrochemistry.

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7. Conflicts of Interest

There are no conflicts of interest to declare.

8. References

- 1 B. Bogdanović, R. A. Brand, A. Marjanović, M. Schwickardi and J. Tölle, *J. Alloys Compd.*, 2000, **302**, 36–58.
- 2 G. Streukens, B. Bogdanović, M. Felderhoff and F. Schüth, *Phys Chem Chem Phys*, 2006, **8**, 2889–2892.
- 3 B. Bogdanović, U. Eberle, M. Felderhoff and F. Schüth, *Scr. Mater.*, 2007, **56**, 813–816.
- 4 G. Sandrock, K. Gross and G. Thomas, *J. Alloys Compd.*, 2002, **339**, 299–308.
- 5 K. J. Gross, G. J. Thomas and C. M. Jensen, *J. Alloys Compd.*, 2002, **330–332**, 683–690.
- 6 H.-W. Li, Y. Yan, S. Orimo, A. Züttel and C. M. Jensen, *Energies*, 2011, **4**, 185–214.
- 7 R. H. Pawelke, *The Master Key to the Problem of Reversible Chemical Hydrogen Storage is 12 kJ (mol H₂)⁻¹*, 2021.
- 8 P. Wang, X.-D. Kang and H.-M. Cheng, *J. Appl. Phys.*, 2005, **98**, 074905.
- 9 C. Li, Y. Liu, R. Ma, X. Zhang, Y. Li, M. Gao and H. Pan, *ACS Appl. Mater. Interfaces*, 2014, **6**, 17024–17033.