

The Master Key to the Problem of Reversible Chemical Hydrogen Storage is $12 \text{ kJ (mol H}_2\text{)}^{-1}$

Roland H. Pawelke

This article shows up the intrinsic thermodynamic boundaries to reversible mass transfer on basis of the ideal gas law and classic equilibrium thermodynamics in relation to chemical hydrogen storage. In the event, a global picture of reversible chemical hydrogen storage is unveiled, including an explanation of partial reversibility. The findings of this work help to clarify problems of metal hydride chemistry which otherwise are difficult if not impossible to solve in convergent manner, e.g. why the substitution of 4 mol % Na by K in Ti-doped NaAlH_4 raises the reversible storage capacity by 42 % or the way the dopants take effect in (Rb/K)-co-doped $\text{Mg(NH}_2\text{)}_2/2\text{LiH}$. This work's result is of a wider significance since based on two cornerstones of physical chemistry and particularly for the normative role of hydrogen electrodes to electrochemistry.

1. Introduction

Reversible metal hydrides for hydrogen storage¹⁻⁴ are a means for reducing the pV -energy inside a pressurized gas storage container,^{5,6} and since consuming heat in hydrogen release,⁷ may put the waste heat of a fuel cell to good use.⁸ Metal hydrides fundamentally separate into reversible and irreversible systems, distinguished by whether the heat tone ΔH of the hydrogenation reaction is negative (reversible) or positive (irreversible). Reversible metal hydrides can be fully or partially reversible, for the latter phenomenon a sound and comprehensive explanation is pending to date. By principle, they file in three main subaltern classes, characterized by the mode respective strength of hydride bonding: interstitial, complex and salt-like hydrides.^{1-4,9,10} Globally, reversible chemical hydrogen storage may be understood by means of a thermodynamic two-phase gas-sorbent equilibrium system in which only one degree of freedom exists, according to the phase rule of Gibbs. By principle, either pressure or temperature can be set freely: the other quantity adjusts accordingly, which provides the means for mediating the storage process. Hydrogen behaviour may be approximated as ideal in the typical temperature-pressure domain of reversible metal hydride sorption reactions ($T > 300 \text{ K}$ and $p < 100 \text{ bar}$). While the ideal gas law and equilibrium thermodynamics are cornerstones of physical chemistry, the full significance of their interrelation for reversible chemical mass transfer seems to have eluded a wider, if any at all, recognition. The essence of reversible chemical hydrogen storage may be captured in an image based on mass transfer: a pressure and/or temperature change creates a chemical potential gradient between the two phases of the system, a thermodynamic driving force ΔG_m . The system reacts to that disturbance of equilibrium by according mass (hydrogen) transfer from one phase to the other, dissipating the gradient in the event, until the new equilibrium phase composition in the system is reached. While this base regularity between equilibrium composition and free enthalpy is not controversial, much less so is the question what it really means: since the chemical potential gradient represents the enthalpy reservoir for the transfer of mass, the question is consequential how the mass of the migrating species relates to

the decrease of the ΔG_m gradient if transferred. A closed, general answer to this question is best possible on basis of the ideal gas law, thus applicable to chemical hydrogen storage. While it for the moment may not be evident how that relation can be quantified, nonetheless the conclusion is compelling that by principle an intrinsic constraint to thermodynamic equilibrium mass transfer exists.

The above image is formulated for hydrogen respective neutral particles, yet virtually all it takes to extend that image to rechargeable batteries is attaching charge to the migrating species and substitute electrical potential in lieu of chemical potential. An according mass transfer understanding is organic to the general perception of electrochemistry as the common unit of Ah kg^{-1} betrays, i.e. for how long a current of ions may be sustained (in relation to a certain potential threshold) by the kg of some reference system, e.g. battery mass. However, this partial unit to specific energy employed with practical scope can get only part of the full image. Yet it is remarkable that the base relation between chemical potential and mass transfer is evidently a generally accepted fundamentality in electrochemistry while the idea of an intrinsic thermodynamic constraint to reversible hydrogen storage capacity – essentially the flipside of the selfsame item – never made much for scientific consensus to date, rather the contrary is true. However, the electrochemistry parallel hints a dismissive attitude to be incorrect, as do partially reversible metal hydrides, as does the wealth of experimental results from decades of R&D suggesting at least some kind of limiting regularity to the reversible chemical hydrogen storage process. Yet these arguments may be all judged indications, not hard evidence: so for settling the matter a demonstration on basis of the 19th century cornerstone fundamentals of physical chemistry is due which this paper is prepared to do.

2. Methodical Approach

The description of a reversible two-phase ideal gas-sorbent equilibrium system is approachable from either the gas or sorbent phase end: opting for the gas phase is somewhat unorthodox but has two big advantages: *first*, an ideal gas is incomparably easier to describe than solid matter: yet there is

full information equivalency at the thermodynamic system level because of the equilibrium relation. *Second*, an intrinsic universality is organic to the approach since the hydrogen gas phase is compellingly a common feature to all hydrogen storage systems whereas a specific sorbent is not. A first reward from adopting the gas phase-centred vantage point is a structured overview of reversible chemical hydrogen storage. The individual metal hydride material classes undoubtedly have their physicochemical peculiarities, however at large they all correspond to a certain domain of hydrogen gas chemical potential, reflecting in the mode respective strength of hydride bonding. This suggests by principle a continuum of reversible physicochemical hydrogen storage materials, from low-temperature adsorbents to high-temperature metal hydrides. The thermodynamic reaction parameters ΔH and ΔS of a reversible metal hydride respective reversible hydrogen sorbent may be derived by means of the van't Hoff equation, shown in equation 1 for the desorption reaction ($\Delta H > 0$): it derives from the chemical potential of an ideal gas and the 2nd law of thermodynamics and provides the equilibrium pressure p_{eq} above the sorbent at a certain temperature T .¹¹

$$\ln\left(\frac{p_{eq}}{p^\circ}\right) = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (1)$$

By principle, the thermodynamics of the sorbent are determined by means of those of the ideal gas phase in equilibrium: the emphasized approach is thus far from being new. Consequently, ΔH and ΔS refer to the mol H_2 and since determined by means of a linear interpolation towards equilibrium at $p^\circ = 1$ bar pressure, they actually have an intrinsic reference to that standard state. Thus, the quotient $\Delta H/\Delta S$ yields the temperature T_{1bar} for an equilibrium pressure of 1 bar, a material-specific constant. A feature of little, if any recognition is $-\Delta H$ having the connotation of an ideal gas phase chemical potential μ_{H_2} : equation 2 is another form of equation 1, featuring the 2nd law of thermodynamics.

$$RT \ln\left(\frac{p^\circ}{p_{eq}}\right) = \Delta H - T\Delta S = (\mu^\circ - \mu) = -\mu_{H_2} \quad (2)$$

Equation 2 shows also with $(\mu^\circ - \mu)$ the negative definition of an ideal gas phase chemical potential $-\mu_{H_2}$; equation 3 subsumes previous equations 1 and 2 accordingly.

$$\ln\left(\frac{p^\circ}{p_{eq}}\right) = \frac{\Delta H}{RT} - \frac{\Delta S}{R} = \frac{-\mu_{H_2}}{RT} \quad (3)$$

As the reversible transition $p_{eq} \leftrightarrow p^\circ$ in relation to temperature is organic to equation 1, forming the derivative of equation 3 with respect to temperature is due, revealing that $-\Delta H$ of the sorbent ($\Delta H > 0$) is equal to μ_{H_2} , as shown in equation 4.

$$\frac{d(\ln(p^\circ/p_{eq}))}{dT} = \frac{-\Delta H}{RT^2} = \frac{\mu_{H_2}}{RT^2} \Rightarrow -\Delta H = \mu_{H_2} \quad (4)$$

Equation 4 tells that if a discharged reversible hydrogen sorbent is placed into a hydrogen gas phase at $p^\circ = 1$ bar, its presence results in the absorption of hydrogen, causing an excursion of the gas phase chemical potential from μ° by μ_{H_2} equal to the negative desorption (synonymous to absorption)

enthalpy $-\Delta H$. Equivalence of ΔH to a chemical potential respective free enthalpy is not a contradiction in a reversible thermodynamic process because by definition ΔG is virtually zero yet infinitesimally negative so there can be a reaction for which $\Delta H = T\Delta S$ applies nonetheless. Re-establishing a pressure of 1 bar above the sorbent requires the higher temperature T_{1bar} which is given by $\Delta H/\Delta S$. This leads to the realization that the van't Hoff ΔH scale offers a way for ranking all reversible hydrogen sorbents by their featured gas phase chemical potential excursion from μ° . Figure 1 sketches how the relation $-\Delta H = \mu_{H_2}$ can be exploited for information about the maximum attainable reversible mass transfer if the logarithmic van't Hoff ΔH scale is a) linearly calibrated to b) the chemical potential shift attributable to the transfer of 1 % w/w H from an absolute origin of zero mass transfer. This is done by means of a reference chemical potential $\mu_{1\%H}^\circ$ that must be moored to IUPAC Standard Temperature and Pressure (STP) which provides two thirds the information required for its definition. The emphasis of molar mass and not volume is due because of its independence from temperature.

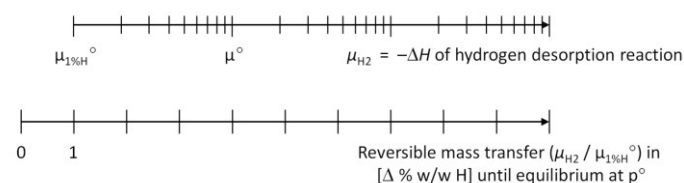


Figure 1 Schematic display of how the logarithmic van't Hoff ΔH scale may be linearly calibrated for information about the maximum reversible mass transfer by means of a reference chemical potential $\mu_{1\%H}^\circ$, attributable to the transfer of 1 % w/w H from an absolute origin of zero mass transfer.

Equation 5 formalizes the postulated linear relation between the quantities $-\Delta H$ respective μ_{H_2} , $\mu_{1\%H}^\circ$ and transferred mass.

$$\frac{-\Delta H}{\mu_{1\%H}^\circ} [1 \% \text{ w/w H}] = \frac{\mu_{H_2}}{\mu_{1\%H}^\circ} [1 \% \text{ w/w H}] \quad (5)$$

The linear-logarithmic proportionality issue implicit to equation 5 may be approached via the fundamental relation $\log_a(x)/\log_a(y) = \log_y(x)$ for changing the logarithmic base, which is illustrated by the example of the ideal hydrogen gas chemical potential at 0.005 bar and $T^\circ = 273.15$ K. Seeing the pressure of 0.005 bar as $0.005 \cdot p^\circ$ and expressing 0.005 as logarithm to a different base, e.g. the golden ratio $\Phi \approx 1.618$, thus 1.618^X with $X = -11.011 \approx -11$ allows for eliminating p° pressure as a factor in the \ln -term, as shown in equation 6.

$$\begin{aligned} \mu_{0.005 \text{ bar}, 273 \text{ K}} - \mu^\circ &= R T^\circ \ln\left(\frac{1.618^X p^\circ}{p^\circ}\right) \mid X = -11; T^\circ = 273.15 \text{ K} \\ &= X R T^\circ \ln(1.618) \end{aligned} \quad (6)$$

As a hypothesis, the chemical potential expressed in this particular way of equation 6 is assumed to be $\mu_{1\%H}^\circ$: a division

of another chemical potential μ_{H_2} respective $-\Delta H$ by it in the sense of equation 5 is sketched in equation 7, with the (p/p°) -term to μ_{H_2} abbreviated as $\{p\}$ and implicit reference to μ° .

$$\frac{-\Delta H}{\mu_{1\%H}^\circ} [1\% \text{ w/w H}] = \frac{\mu_{H_2}}{\mu_{0.005 \text{ bar}, 273 \text{ K}}} [1\% \text{ w/w H}] = \frac{RT \ln\{p\}}{RT^\circ X \ln(1.618)} [1\% \text{ w/w H}] \quad | \quad X = -11; T^\circ = 273.15 \text{ K} \quad (7)$$

Equation 7 contains with T/T° a Charles' law proportionality term but it is expedient to substitute by the ideal gas law for $T = pV_m/R$. The negative arithmetic sign of X cancels out with those in the numerator ($-\Delta H$, $\Delta H > 0$), as do the universal gas constants. Equation 8 shows the result of the transformations.

$$\frac{-\Delta H}{\mu_{1\%H}^\circ} [1\% \text{ w/w H}] = \frac{\mu_{H_2}}{\mu_{0.005 \text{ bar}, 273 \text{ K}}} [1\% \text{ w/w H}] = \frac{p V_m}{p^\circ V_m^\circ} \frac{Y}{X} [1\% \text{ w/w H}]$$

$$p^\circ = 1 \text{ bar} \quad T^\circ = 273.15 \text{ K} \quad V_m^\circ = 22.71 \text{ L}$$

$$Y = \log_{1.618}\{p\} \quad X = 11 \quad (8)$$

Equation 8 demonstrates that a division operation in the sense of equation 5 results in proportionality indeed, showing in an ideal gas pV_m -energy proportionality term multiplied with a proportionality term (Y/X) comprising of the logarithms to the base of Φ . Therefore, if the constituting pressure of $\mu_{1\%H}^\circ$ is understood in the sense of the above example, a mere division linearly calibrates any $-\Delta H$ enthalpy respective μ_{H_2} by means of the fundamental logarithmic law $\log_a(x)/\log_a(y) = \log_y(x)$. This law further suggests the actual nature of that new logarithmic base being beyond scope as not vital to the demonstration of the principal viability of equation 5. With that point settled, the definition of the ideal gas chemical reference potential $\mu_{1\%H}^\circ$ is approached: because moored at IUPAC Standard Temperature and Pressure (STP), temperature is set to $T^\circ = 273.15 \text{ K}$ and one end of its pressure gradient fix at p° . So the tricky task is the assessment of the remaining pressure since this way the quality of first increment 1 % w/w H mass transfer needs to be captured with general validity.

3. Results

Thermodynamics are by their nature an entirely relative affair, structured around a standard state and intriguingly, solving the issue at hand demands to mark out an absolute origin which may not seem feasible within that fundamentally relative conception. But what actually defines that absolute zero reference point in the mass transfer context? It must be the maximum possible off-equilibrium distance from the standard potential μ° . This is easy to imagine as a reversible two-phase gas-sorbent system cannot be any more off-equilibrium than all the gas being contained in the sorbent while surrounded by a zero-pressure vacuum. This image is the key towards the definition of $\mu_{1\%H}^\circ$ which constitutes by means of an equilibrium system at a) 273.15 K, comprising of b) 1 gram sorbent, which is c) surrounded by a free volume of 22.71 L,

the molar ideal gas volume at STP, as the excursion from μ° is a cornerstone in the definition of this calibration process and $d\mu = V_m dp$ applies, but d) perfectly evacuated. The sorbent mass is 1 g for the reason it is virtually the atomic mass of the hydride ion respective hydrogen atom and a mol of atomic matter can by definition not weigh less than 1 g. Desorbing 1 % w/w respective 0.01 g of the sorbent as ideal hydrogen gas will create a system pressure of 0.005 bar. That is it, one does not need to know anything specific about that absolute zero-origin to hydrogen mass transfer because the ideal gas chemical potential at 0.005 bar and 273.15 K in the common thermodynamic terminology conveys the information after the fact. So is $\mu_{1\%H}^\circ$ a quantity of general validity? Yes, it is because of the irreducible reference to the mass of the hydrogen atom, hence also encompassing the virtually identical proton and neutron masses. Therefore $\mu_{1\%H}^\circ$ refers to the base mass unit by which the atomic masses of all elements of the periodic table (and thus compounds thereof) scale. Equation 9 shows the value of the ideal hydrogen mass transfer constant $\mu_{1\%H}^\circ$.

$$\mu_{1\%H}^\circ = R \cdot 273.15 \text{ K} \cdot \ln\left(\frac{0.005 \text{ bar}}{1 \text{ bar}}\right)$$

$$= -12033 \text{ J (mol H}_2\text{)}^{-1} [1\% \text{ w/w H}]^{-1} \quad (9)$$

It is reasonable to exploit this result towards a general expression for the maximum equilibrium hydrogen transfer as function of temperature and pressure, which is possible on basis of the data of HEMMES *et al* who tabulated the molar Gibbs enthalpy (i.e. the chemical potential) of hydrogen from 100 K to 1000 K and for pressures up to 1 Mbar;¹² figure 2 shows the pressure-dependency of the isothermal molar Gibbs enthalpy in 100 K increments accordingly. The array of curves fits the general expression shown in equation 10.

$$G_{m,H_2}(T, p) = a(T) \cdot \ln\{p\} - b(T) \quad (10)$$

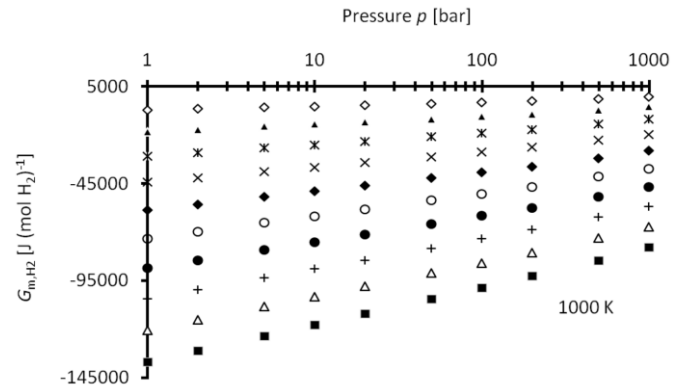


Figure 2 Semi-logarithmic plotting of the isothermal pressure dependency of the molar Gibbs enthalpy of hydrogen on basis of the data by HEMMES *et al*.¹²

The solutions for the coefficients $a(T)$ and $b(T)$ are graphically determined, also available as electronic supplementary information. Equation 11a displays the function for coefficient $a(T)$ which is a linear dependent of temperature.

The temperature dependency of coefficient $b(T)$ can be described by the polynomial function shown in equation 11b, with the terms aligned as vertical sum for the reason of clarity.

$$a(T) = 8.363 \text{ J (mol H}_2\text{)}^{-1} \text{ K}^{-1} \cdot T + 140.447 \text{ J (mol H}_2\text{)}^{-1} \quad (11a)$$

$$b(T) = \begin{array}{rclcl} -2.120 & 10^{-5} & \text{J (mol H}_2\text{)}^{-1} & \text{K}^{-3} T^3 & \\ +6.519 & 10^{-2} & \text{J (mol H}_2\text{)}^{-1} & \text{K}^{-2} T^2 & \\ +9.620 & 10^1 & \text{J (mol H}_2\text{)}^{-1} & \text{K}^{-1} T & \\ -3.065 & 10^3 & \text{J (mol H}_2\text{)}^{-1} & & \end{array} \quad (11b)$$

Equation 10 is now combined with equations 11a and 11b for a numerical expression for the molar Gibbs enthalpy of hydrogen as function of pressure and temperature, shown in equation 12: in the typical (T, p) -domain of reversible metal hydride sorption reactions ($p < 100$ bar and $T > 300$ K) is the deviation from the data of HEMMES *et al* below $\pm 1.0\%$.

$$G_{m, H_2}(T, p) = \begin{array}{rclcl} +8.363 & & \text{J (mol H}_2\text{)}^{-1} & \text{K}^{-1} T & \ln\{p\} \\ +1.404 & 10^2 & \text{J (mol H}_2\text{)}^{-1} & & \ln\{p\} \\ +2.120 & 10^{-5} & \text{J (mol H}_2\text{)}^{-1} & \text{K}^{-3} T^3 & \\ -6.519 & 10^{-2} & \text{J (mol H}_2\text{)}^{-1} & \text{K}^{-2} T^2 & \\ -9.620 & 10^1 & \text{J (mol H}_2\text{)}^{-1} & \text{K}^{-1} T & \\ +3.065 & 10^3 & \text{J (mol H}_2\text{)}^{-1} & & \end{array} \quad (12)$$

Division of equation 12 by $-12033 \text{ J (mol H}_2\text{)}^{-1} [1 \% \text{ w/w H}]^{-1} = \mu_{1\%H}^\circ$ yields the maximum equilibrium hydrogen mass transfer in relation to pressure and temperature (equation 13).

$$[\Delta \% \text{ w/w H}](T, p) = \begin{array}{rclcl} -6.950 & 10^{-4} & [1 \% \text{ w/w H}] & \text{K}^{-1} T & \ln\{p\} \\ -1.167 & 10^{-2} & [1 \% \text{ w/w H}] & & \ln\{p\} \\ -1.762 & 10^{-9} & [1 \% \text{ w/w H}] & \text{K}^{-3} T^3 & \\ +5.418 & 10^{-6} & [1 \% \text{ w/w H}] & \text{K}^{-2} T^2 & \\ +7.995 & 10^{-3} & [1 \% \text{ w/w H}] & \text{K}^{-1} T & \\ -2.547 & 10^{-1} & [1 \% \text{ w/w H}] & & \end{array} \quad (13)$$

In equation 13, it is discernible that a pressure below 1 bar causes the \ln -term to change arithmetic sign, resulting in a positive contribution to the maximum reversible storage capacity: this is correct and in line with the experimental reality of desorption at pressures below 1 bar. Based on equation 13, a map of maximum reversible chemical hydrogen storage capacity can be drawn by plotting temperature versus pressure for constant reversible hydrogen storage capacity: figure 3 shows the lines for integer values, it is also available as electronic supplementary information. Under the equilibrium premise, these contour lines mark out the thermodynamic limits to hydrogen mass transfer at the respective (T, p) -condition of a reversible chemical hydrogen storage system.

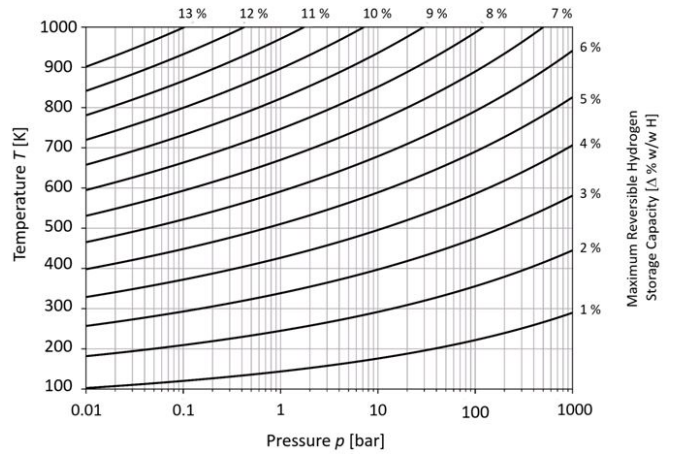


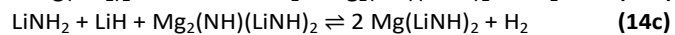
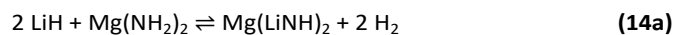
Figure 3 A semi-logarithmic plotting of temperature versus pressure of equation 13 values, revealing the contour lines of constant maximum hydrogen storage capacity.

4. Discussion

From its ideal gas and classic equilibrium thermodynamics foundations towards its result of intrinsic thermodynamic limitation to reversible hydrogen mass transfer, the line of argument is tight; there are no flanks not already covered along the way so there is no need for a discussion of the process as such. The boundaries base on the premise of equilibrium in a two-phase gas-sorbent system and are insofar definite as there cannot be a less hindered mass transfer across phase boundaries than those in the form of the ideal gas. It may surprise that the sorbent phase is a secondary quantity to this consideration and it might outright offend that the sorbent phase properties, commonly deemed decisive and within scientific scope, play no vital part in it at all. That may as it be; because the thermodynamics of the gas phase account for any sorbent phase-related process and series thereof in blanket fashion, information equivalency is assured due to the thermodynamic equilibrium relation – dismissing that point means dismissing the working principle of the van't Hoff equation. Yet said equivalency is not commutative in terms of insight as none of the findings of this work are directly accessible by a sorbent material-focused calculation or experiment respective series thereof: it is the change of perspective that truly makes the difference.

To demonstrate the analytical superiority of the present gas-phase equilibrium approach, its findings are applied to two examples which are among if not the toughest metal hydride hydrogen storage systems to make sense of: these are the (4 mol % RbH/4 mol % KH)-co-doped $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$ system and the (4 mol % KH/4 mol % Ti)-co-doped NaAlH_4 system. Starting with the former, the (4 mol % RbH/4 mol % KH)-co-doped $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$ system is discussed on basis of the multiple-cycle study of Li *et al.*¹³ A feature striking the eye, literally as in the graphical abstract, is that the reversible hydrogen capacity of 4.4 % w/w H is bound to a hydrogenation temperature of 130 °C. If hydrogenated at just 120 °C, there is

a decline in storage capacity, from initially 4.8 % w/w H to stable 3.6 % w/w H within the first eight cycles. However, it increases to stable 4.4 % w/w H if the hydrogenation temperature is raised to 130 °C. This suggests a switch-on temperature at which a new reaction pathways opens up; below, the storage capacity reflects the thermodynamics of the pristine $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$ system which is shown along with its subaltern reactions in equations 14a to 14c.^{14,15}

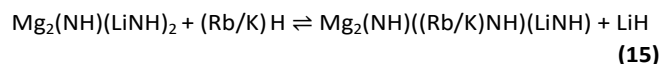


XIONG *et al* report a desorption enthalpy of $44.1 \text{ kJ} (\text{mol H}_2)^{-1}$ for equation 14a,¹⁶ translating to reversible 3.7 % w/w H in terms of the present work and in fine agreement with the above reasoning. For equation 14b, termed plateau region by XIONG *et al*, a desorption enthalpy of $38.9 \text{ kJ} (\text{mol H}_2)^{-1}$ is determined.¹⁶ This suggests in contrast to the statement of Li *et al* that hydrogenation is far from being incomplete but always right at the thermodynamic limit. Reversing the equilibrium approach, the increase of 0.8 % w/w H in storage capacity equals a gain in hydrogen fixation potential of $-8.4 \text{ kJ} (\text{mol H}_2)^{-1}$. The standard formation enthalpy ΔH_f° of LiNH_2 is given with -182 kJ mol^{-1} ,¹⁷ while those of KNH_2 and RbNH_2 are $-128.9 \text{ kJ mol}^{-1}$ and $-113.0 \text{ kJ mol}^{-1}$, respectively.¹⁸ The stabilities of the binary hydrides LiH , KH and RbH file likewise with formation enthalpies of $-90.5 \text{ kJ mol}^{-1}$, $-57.7 \text{ kJ mol}^{-1}$ and $-52.3 \text{ kJ mol}^{-1}$, respectively.¹⁸ The formation enthalpy of magnesium amide figures to $-167.1 \text{ kJ mol}^{-1}$ based on those of MgH_2 ($-75.3 \text{ kJ mol}^{-1}$) and NH_3 ($-45.9 \text{ kJ mol}^{-1}$).¹⁸ Evidently, the $-8.4 \text{ kJ} (\text{mol H}_2)^{-1}$ in additional hydrogen fixation potential must be discernible in at least one Li- metathesis reaction attributable to the doping modification and because there is an accompanied catalytic effect, a closed stoichiometric cycle is a further requirement: Thus, the sum of all partial equations must yield the reaction of the pristine system yet at the same time allow for a clear distinction at some point from it.

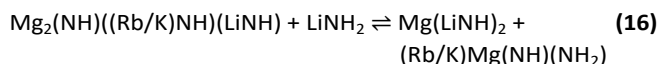
Since RbH and KH show similar formation enthalpies, the following reasoning refers to a hypothetical average (Rb/K) cation. With regard to equations 14b and 14c, the first metathesis must be an exchange between some Li- imide reactant and $(\text{Rb/K})\text{H}$ resulting in the formation of LiH because RbNH_2 respective KNH_2 cannot be formed from LiNH_2 since the resulting enthalpy gap is too large for compensation by LiH formation, this applies in kind for $\text{Mg}(\text{NH}_2)_2$ either. However, in the first elementary reaction of equation 14b there is no opportunity for that as it yields the first Li- imide reactant.



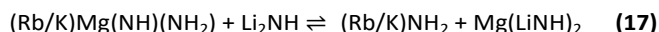
The product $\text{Mg}_2(\text{NH})(\text{LiNH})_2$ offers a first opportunity for said formation of LiH in a metathesis reaction (equation 15).



$\text{Mg}_2(\text{NH})((\text{Rb/K})\text{NH})(\text{LiNH})$ may exchange with LiNH_2 in analogy to equation 14c for the product $\text{Mg}(\text{LiNH})_2$ of equation 14c, as shown in equation 16.



The existence of $\text{RbMg}(\text{NH})(\text{NH}_2)$ is verified,¹⁹ it is isostructural to its potassium analogue.²⁰ Both phases are expected to play a vital role in the beneficial effects associated with KH and RbH doping of $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$.^{21,22} Reaction of $(\text{Rb/K})\text{Mg}(\text{NH})(\text{NH}_2)$ with lithium imide,²³⁻²⁸ leads to $(\text{Rb/K})\text{NH}_2$ and a further equivalent of $\text{Mg}(\text{LiNH})_2$, shown in equation 17.



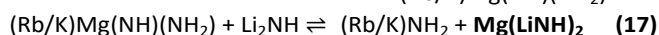
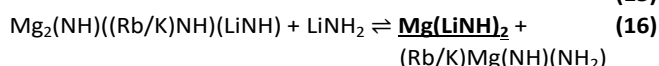
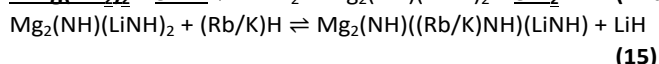
A source of lithium imide is the reaction of equation 18, in its own right a system capable of storing hydrogen at a ΔH of $\pm 67 \text{ kJ} (\text{mol H}_2)^{-1}$,²⁹⁻³¹ the reversible storage capacity is 5.5 % w/w H,³² exactly as the prediction on basis of this work goes. It is part of the pristine $\text{Mg}(\text{NH}_2)_2/2\text{LiH}$ system as equation 14c and multiple works suggest.²³⁻²⁸



The large formation enthalpy of LiNH_2 of $\Delta H_f^\circ = -182 \text{ kJ mol}^{-1}$ favors the metathesis reaction between $(\text{Rb/K})\text{NH}_2$ and LiH which regenerates the catalyst and closes the reaction cycle, shown in equation 19.



The reaction of equation 19 is irreversible and provides the additional thermodynamic potential for binding the surplus- to- equilibrium hydrogen amount. Thus, the complete reaction system may be set up by combining equation 14b with equations 15 to 19; except for the bold underlined reactants, all other cancel out and in sum equation 14a is obtained.



In order to figure the additional hydrogen fixation potential resulting from the doping, taking the mean formation enthalpy of KNH_2 and RbNH_2 is sensible with regard to equation 19. $(\text{Rb/K})\text{NH}_2$ has a mean formation enthalpy of $-121.0 \text{ kJ mol}^{-1}$, likewise the average formation enthalpy of $(\text{Rb/K})\text{H}$ is $-55.0 \text{ kJ mol}^{-1}$. The formation enthalpy of LiH figures to $-90.5 \text{ kJ mol}^{-1}$ and consequently, the enthalpy balance between right and left side of equation 19 yields a gain of $-25.5 \text{ kJ mol}^{-1}$. This enthalpy difference refers to the three mol of hydrogen of equation 14b since the single mol hydrogen generated by equation 18 occurs in a pathway that is also vital to the pristine system as equation 14c suggests. Therefore, it is not relevant for the difference between (Rb/K) -doped and pristine system and the $-25.5 \text{ kJ mol}^{-1}$ enthalpy difference needs to be

divided by three for the correct reference to the mol hydrogen. This yields an additional hydrogen fixation potential of $-8.5 \text{ kJ (mol H}_2\text{)}^{-1}$, in excellent agreement with the theoretical prediction of $-8.4 \text{ kJ (mol H}_2\text{)}^{-1}$. Since the doping process affects only equation 14b, its desorption enthalpy of $+38.9 \text{ kJ (mol H}_2\text{)}^{-1}$ is reduced by the additional hydrogen fixation potential of $-8.4 \text{ kJ (mol H}_2\text{)}^{-1}$ multiplied with the total pathway concentration of 8 mol %. The desorption enthalpy per mol hydrogen is thus expected to be $0.672 \text{ kJ (mol H}_2\text{)}^{-1}$ smaller than $38.9 \text{ kJ (mol H}_2\text{)}^{-1}$, hence $38.23 \text{ kJ (mol H}_2\text{)}^{-1}$. Li *et al* measure by DSC two overlapping endothermic peaks of $38.1 \pm 0.4 \text{ kJ (mol H}_2\text{)}^{-1}$ and $38.4 \pm 0.4 \text{ kJ (mol H}_2\text{)}^{-1}$ which belong to the reversible hydrogen release reactions. The arithmetic mean of these experimental values yields $38.25 \text{ kJ (mol H}_2\text{)}^{-1}$ for the hypothetical joint (Rb/K)-catalyzed reaction. This is a mere 0.5 per thousand away from the value of $38.23 \text{ kJ (mol H}_2\text{)}^{-1}$ derived on basis of the findings of this work.

Regarding the second example, the substitution of 4 mol % sodium by potassium in 4 mol % Ti-doped NaAlH_4 is a work by WANG *et al.*³³ This rather small modification raises the reversible storage capacity from 3.3 % w/w H to 4.7 % w/w H, a massive increase by 42% while the desorption enthalpy ΔH changes by less than 5%. Considering 4 mol % Ti-doped NaAlH_4 the baseline equilibrium case, WANG *et al* report for the hydrogen capacity of 3.3 % w/w H a desorption enthalpy of $\Delta H = 40.57 \text{ kJ (mol H}_2\text{)}^{-1}$; while reasonably close to the reference value of $40.05 \text{ kJ (mol H}_2\text{)}^{-1}$ by BOGDANOVIĆ *et al.*,³⁴ it must be critically mentioned that the latter is the average of both sorption reactions and thus the more complete one. However, the resulting difference in terms of predicted hydrogen storage capacity is rather small, 3.37 % w/w H versus 3.33 % w/w H which may be altogether called a fine agreement of theory to experiment. So what about the massive increase in storage capacity by 42% resulting from the co-doping with potassium? The desorption enthalpy of that system is with $38.90 \text{ kJ (mol H}_2\text{)}^{-1}$ actually *smaller* than those of the baseline equilibrium case. So it is substantially more hydrogen capacity at less desorption enthalpy – does that disprove the equilibrium approach? Not at all, on the contrary; the reason for that has been already encountered in the (4 mol % RbH/4 mol % KH)-co-doped $\text{Mg(NH}_2\text{)}_2/2\text{LiH}$ system: an additional hydrogen fixation potential is of negative arithmetic sign, contrary to those of the desorption enthalpy. Consequently, a system co-doped for a higher hydrogen capacity shows a smaller apparent desorption enthalpy in comparison to the baseline equilibrium system. In this specific case, it is chemically reasonable to relate the gain in hydrogen capacity to the next stable mixed potassium-sodium aluminum hydride K_2NaAlH_6 (as KNa_2AlH_6 is thermodynamically instable).³⁵ GRAETZ *et al* give the desorption enthalpy of K_2NaAlH_6 with $97 \text{ kJ (mol H}_2\text{)}^{-1}$;³⁶ relating that value to the ΔH reference of $47 \text{ kJ (mol H}_2\text{)}^{-1}$ for $[\text{AlH}_6]$ desorption by BOGDANOVIĆ *et al.*,³⁴ the difference in hydrogen fixation potential between Na_3AlH_6 and K_2NaAlH_6 estimates to: $47 \text{ kJ (mol H}_2\text{)}^{-1} - 97 \text{ kJ (mol H}_2\text{)}^{-1} = -50 \text{ kJ (mol H}_2\text{)}^{-1}$. Adjustment to the 2:1 ratio between $[\text{AlH}_4]$ and $[\text{AlH}_6]$ stages in the NaAlH_4 system yields $-16.7 \text{ kJ (mol H}_2\text{)}^{-1}$ which

corresponds to a gain of 1.39 % w/w H in reversible hydrogen capacity, a fine agreement with the result of WANG *et al.*

This exemplary outline shows that the equilibrium approach works fine in predicting the reversible hydrogen capacity of an equilibrium system by means of the featured reaction enthalpy ΔH . However, said equilibrium capacity can be exceeded by doping for a reversible metal hydride of a higher reaction enthalpy. The mere fact *that* the equilibrium approach can be applied with great effect also for figuring the effects of co-doping on the equilibrium system suggests that doping and the base equilibrium system work by the selfsame principle(s).

While it is evident that the equilibrium approach gets much right it does not capture the complete picture as leaving open how a surplus-to-equilibrium hydrogen amount introduced by doping is retained in the sorbent phase, leading towards two concluding statements about the matter: *first*, doping is a means for accessing the (T, p) -boundaries to hydrogen storage capacity marked out in figure 3. *Second*, because doping leaves the thermodynamic reaction parameters of the equilibrium system comparably unaffected, the retention of surplus-to-equilibrium hydrogen must base on something principally different from ΔH equilibrium considerations.

While that already anticipates the essence of the likely answer, it is scope for another day's work.

5. Conclusions

1. Approaching reversible chemical hydrogen storage by means of a two-phase gas-sorbent equilibrium model and from an ideal gas phase bias unveils a global view on the reversible physicochemical hydrogen storage process.
2. That equilibrium approach ultimately allows the determination of thermodynamic limits to ideal reversible mass transfer i.e. hydrogen storage capacity in relation to temperature and pressure.
3. Towards that end, the calibration of the van't Hoff ΔH scale for reversible mass transfer is instrumental which bases on two features of equilibrium thermodynamics: *first*, the negative metal hydride desorption enthalpy $-\Delta H$ is equivalent to a featured excursion μ_{H_2} of the gas phase chemical potential from μ° . *Second*, said μ_{H_2} can be exploited for the information about the possible ideal mass transfer in $[\Delta\% \text{ w/w H}]$ if linearly calibrated by a mass transfer constant $\mu_{1\% \text{H}}^\circ$, which is a meaningfully defined ideal gas chemical potential, figuring to $-12033 \text{ J (mol H}_2\text{)}^{-1} [1\% \text{ w/w H}]^{-1}$.
4. This approach allows far-reaching yet convergent conclusions in the analysis of metal hydride systems as demonstrated by the examples of two difficult to understand examples: (4 mol % RbH/4 mol % KH)-co-doped $\text{Mg(NH}_2\text{)}_2/2\text{LiH}$ and (4 mol % KH/4 mol % Ti)-co-doped NaAlH_4 .
5. The equilibrium approach works well for assessing the hydrogen storage capacity of the base ΔH equilibrium reaction case which however may be exceeded if that

- system is doped for a metal hydride of a higher formation enthalpy. That the equilibrium approach can be also used for figuring out the impact of doping on the equilibrium system implies that both work by the same principle(s).
- However, the equilibrium approach does not reveal how that surplus-to-equilibrium hydrogen amount may be retained in the sorbent phase. While doping is a means for accessing the (T, p) -boundaries to hydrogen storage capacity, the retention of such a surplus-to-equilibrium hydrogen amount must base on something principally different from ΔH equilibrium considerations.
 - By principle, the findings of this work must also apply to electrochemistry due to the normative role of hydrogen electrodes to it.

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7. Conflicts of interest

There are no conflicts to declare.

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