The Key to the Problem of Reversible Chemical Hydrogen Storage is 12 kJ (mol H₂)¹

Roland H. Pawelke

This article outlines a simple theoretical formalism illuminating the boundaries to reversible solid hydrogen storage, based on the ideal gas law and classic equilibrium thermodynamics. A global picture of chemical reversible hydrogen sorption is unveiled, including a thermodynamic explanation of partial reversibility.

Introduction

Batteries do not scale with unchallenged efficiency into the domain of tens of kW rated power output and MWh energy storage demand. In storing energy for applications of such and beyond, (reversible) fuel cell²⁻³ energy systems may emerge as preferred solution,³,⁴ especially if the envisaged usage time measures in decades and human life-support is a requirement. Notable examples are manned spaceflight⁵⁻⁶ and air-independent propulsion systems of submarines⁶⁻⁷. Reversible metal hydrides for hydrogen storage⁸⁻¹¹ are a means for reducing the pV-energy inside a pressurized gas storage container,¹²⁻¹³ and since consuming heat in the hydrogen release,¹⁴ take harmoniously advantage of the waste heat from the fuel cell.¹⁵

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). In between lie those metal hydrides of partial reversibility, showing reversible hydrogen storage capacities that fall short of the nominal hydrogen content by reaction stoichiometry.

Reversible metal hydrides file in three major sub-classes by mode of hydrogen bonding (in rising order of stability): interstitial, complex and salt-like which however show beyond the ability of reducing hydrogen to hydride chemically at least as much differences as similarities to each other.⁸⁻¹¹,¹⁶⁻¹⁷ Hydrogen storage in reversible metal hydrides represents a case of a thermodynamic two-phase gas-sorbent equilibrium system, which has only one degree of freedom according to the phase rule of Gibbs. Furthermore, hydrogen can be reasonably well approximated as an ideal gas in the temperature and pressure domain of reversible metal hydrides (T > 200 K, p < 200 bar).

To the author’s best of knowledge and surprise, the implications of this concert on thermodynamic system level never saw full outline in the publication-rich history of solid hydrogen storage. The thermodynamics of a two-phase gas-sorbent system allow only the free setting of either pressure or temperature: the other quantity follows suit unless restrained by available substance amount (kinetic hindrance from scope excluded).

Such a two-phase equilibrium system self-adjusts to a pressure or temperature disturbance by a mass transfer between the phases until the chemical potentials of both are equal again. A non-equilibrium hydrogen content in either the gas or sorbent phase results in a molar free Gibbs enthalpy difference ΔGₘ resulting in mass transfer and upon reaching thermodynamic equilibrium for ΔGₘ = 0, the gas sorption reaction, whichever direction, macroscopically stops. Therefore, the under distinct (T, p) – conditions maximum possible reversible hydrogen transfer between both phases is bound to ΔGₘ.

The description of a reversible two-phase gas-sorbent system is approachable from either the gas or sorbent phase end. Opting for the gas phase is unorthodox but has two advantages: first, an ideal gas is incomparably simpler to describe than solid matter, yet there is full information equivalency at the gas-sorbent system level due to the equilibrium relation. Second, this entails an intrinsic universality since the hydrogen gas phase is compellingly a common feature to all reversible solid hydrogen storage systems while the sorbent is not. A first reward from adopting the gas phase vantage point is a self-revealing comprehensive explanation why the different levels of stability observed for metal hydrides relate to different hydrogen bonding principles while globally sharing just about the capability of binding hydrogen as hydride to the solid state. This is plausible since binding hydrogen reversibly to the solid state at different gas phase chemical potential levels requires different bond strengths respective bonding principles.

Methodical Approach

The thermodynamic reaction data ΔH and ΔS of a reversible metal hydride respective hydrogen sorbent are commonly determined via the van’t Hoff equation, shown in equation 1 for the desorption reaction (ΔH positive).¹⁸

\[
\ln \left( \frac{p}{p^°} \right) = \frac{-ΔH}{RT} + \frac{ΔS}{R}
\]

(1)

ΔH and ΔS of a hydrogen sorbent refer to the mole H₂ and are determined by a linear interpolation towards equilibrium at p* = 1 bar pressure under the tacit premises of a) both being constant over temperature and b) the transition p ↔ p* as function of temperature occurring in a reversible thermodynamic process.

A feature of little, if any at all, recognition is −ΔH having the connotation of an ideal gas phase chemical potential µ_H₂ in this transition. Equation 2 is an alternate writing of equation 1, showing the definition of the chemical potential of an ideal gas encompassing the second law of thermodynamics.

\[
RT \ln \left( \frac{p}{p^°} \right) = ΔH - TΔS = (µ^* - µ) = -μ_H₂
\]

(2)
Equation 2 contains with \((\mu^* - \mu)\) the negative definition of an ideal gas phase chemical potential. Equation 3 subsumes previous equations 1 and 2.

\[
\ln \left(\frac{p}{p^*}\right) = -\frac{\Delta H}{R} + \frac{\Delta S}{R} = \frac{\mu_{i2}}{R} T
\]

(3)

In order to describe the reversible transition \(p \leftrightarrow p^*\) implicit to equation 1, forming the derivative of equation 3 with respect to temperature is due, shown in equation 4 under the premises of constant system volume and substance amount.

This reveals \(-\Delta H\) of the sorbent (\(\Delta H\) positive) being equal to \(\mu_{i2}\).

\[
\frac{d \ln (p/p^*)}{dT} = -\frac{\Delta H}{R} T^2 = \frac{\mu_{i2}}{R} T^2 \quad \Rightarrow \quad -\Delta H = \mu_{i2}
\]

(4)

Considering the change following the insertion of a discharged reversible sorbent into a pristine hydrogen gas phase at 1 bar, the presence of the sorbent induces via hydrogen absorption an excursion of the gas phase chemical potential from \(\mu^*\) by \(-\mu_{i2}\) equal to the desorption enthalpy \(\Delta H\).

This equivalency is not contradictory in a reversible process for which \(\Delta G\) is infinitesimally negative yet virtually zero and \(\Delta H = T\Delta S\) applies throughout the transition. For at ambient temperature stable metal hydrides, re-establishing a pressure of 1 bar above the sorbent requires the (higher) temperature \(T_{1\text{bar}} = \Delta H/\Delta S\). This makes the van't Hoff \(\Delta H\) scale a tool for ranking all possible reversible hydrogen sorbents by their featured excursion \(\mu_{i2}\). The chemical potential \(\mu_{i2}\) describes the dependency of the Gibbs enthalpy from substance amount and marks the maximum available isothermal \(pV\)-energy exploitable as volume work along a pressure gradient relative to 1 bar.

Figure 1 shows how the relation \(-\Delta H = \mu_{i2}\) can be exploited for information about the maximum possible reversible mass transfer until equilibrium at 1 bar is reached if the logarithmic van't Hoff \(\Delta H\) scale is a) linearly calibrated to b) the chemical potential shift attributable to the transfer of 1 % w/w H between sorbent and gas phase. This new reference chemical potential is designated as \(\mu_{i2}\) in order to distinguish it from \(\mu^*\). For general validity, emphasis of mass and not volume is due since the former is independent of temperature.

Equation 5 displays the envisaged linear relation between the maximum reversible hydrogen storage capacity of a hydrogen sorbent, the reversible desorption reaction enthalpy \(\Delta H\) of a metal hydride and \(\mu_{\text{iH}}^{\text{max}}\).

\[
\frac{-\Delta H}{\mu_{\text{iH}}^{\text{max}}} = \frac{\mu_{i2}}{\mu_{\text{iH}}^{\text{max}}} \left[1 \% \text{ w/w H}\right]_{\text{rev, max}}
\]

(5)

The feasibility of the linear-logarithmic transformation implicit to equation 5 is demonstrated by the example of the chemical potential for the pressure gradient between 0.005 bar and 1 bar at 273.15 K. The figure 0.005 is expressible as power to the golden ratio \(\Phi \approx 1.618\), as 1.618\(^4\) with \(X = -11.01036 \approx -11\). This transformation eliminates the logarithm of pressure as variable as displayed in equation 6.

\[
\mu_{0.005 \text{bar}} - \mu^* = X T \ln \left(\frac{1.618 \cdot p^*}{p^*}\right) \text{ with } X = -11
\]

(6)

Since the chemical potential \(\mu\) represents the maximum available isothermal \(pV\)-energy exploitable as volume work, the expansion must result for an ideal gas in a full conversion to entropy. Averaging of \(\mu_{0.005}\) by \(X\) must therefore yield the arithmetic mean of the isothermal entropies of hydrogen gas at the respective pressures of the gradient. For a temperature of \(T = 273.15 \text{ K}\) combine all constants to 1093 J (mol H\(_2\))\(^3\) and division by \(X = -11\) yields \(-99\) J (mol H\(_2\))\(^1\) for the mean molar entropy between 0.005 bar and 1 bar pressure. Due to the symmetry of the In-function the negative of \(-99\) J (mol H\(_2\))\(^1\) is the reciprocal of the quotient in the In-pressure term (200 bar). Interpolating the arithmetic mean entropy of 1 bar and 200 bar at 273.15 K from tabulated thermodynamic hydrogen data yields in fine agreement 99 J (mol H\(_2\))\(^1\).

This example features the changing of the base of the In-term from \(e\) to \(\Phi\) via the basic relation \(\log_e (x) / \log_e (\Phi) = \log_\Phi (x)\). The unique qualities of \(\Phi\), also showing in the golden number sequence respective \(\Phi^y/\Phi^x = \Phi^{y-x}\), can be exploited to create proportionality between \(\mu_{i2}\) and \(\mu_{\text{iH}}^{\text{max}}\) in a division operation in the kind of equation 5 if \(\mu_{\text{iH}}^{\text{max}}\) the In-pressure term is transformed accordingly to \(p = \Phi^x p^*\). The direct proportionality of equation 5 resulting from this transformation must become visible in an extractable quotient of logarithms \((Y/X)\) to the base of \(\Phi\). \(\mu_{\text{iH}}^{\text{max}}\) encompasses self-evidently the IUPAC Standard Pressure and Temperature (STP) condition at 273.15 K and 1 bar for general compliance what places \(\mu_{\text{iH}}^{\text{max}}\) at \(T^* = 273.15 \text{ K}\) and sets one end of its pressure gradient to \(p^* = 1 \text{ bar}\). The tricky task is the meaningful definition of the remaining pressure, as it is there where the quality of 1 % w/w H reversible mass exchange between gas and sorbent phase with general validity must materialize.

Results

In order to transform the logarithmic van't Hoff \(\Delta H\) scale into a linear number line of reversible storage capacity, \((\mu_{\text{iH}}^{\text{max}} - \mu^*)\) must mark out its origin. This entails that the mass transfer of 1

Figure 1. Schematic display of the envisaged recalibration of the van't Hoff scale to yield information about the maximum reversible mass transfer possible before equilibrium at 1 bar is reached (this requires furthermore the molecular weight of the gas and the sensible definition of the reference mass for the sorbent).
% w/w H must occur at the maximum possible off-equilibrium distance from \( \mu^* \). A 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. The molecular mass of the hydrogen atom is virtually equal to those of protons and neutrons, and thus represents the standard by which the atomic masses of all other elements scale. Therefore, 1 gram as the mass of 1 mole of hydrogen atoms respective 1 mole of nuclear particles is the reference for the mass transfer of 1 % w/w H. It is discernible that the chemical potential \( \mu_{298ºK}^* \) does actually not describe the reversible transfer of 1 % w/w hydrogen atoms between the two phases but 1 % w/w of nuclear particle mass as (ideal) hydrogen gas! This fine yet fundamental distinction constitutes the general validity for all possible hydrogen sorbents by the periodic table. The system constituting \( \mu_{298ºK}^* \) is a perfectly evacuated vessel at \( T^* = 273.15 \) K, containing 1 g of hydrogen sorbent and with a free volume of 22.7 L, the molar ideal gas volume at \( p^* \) and this temperature. This 1 gram of sorbent reversibly releases 1 % w/w as hydrogen gas into the vacuum, corresponding to 0.01 g or 0.005 mol H\(_2\). This results in a pressure increase from zero-vacuum to 0.005 bar due to the boundary conditions. The pressure gradient between 0.005 bar and 1 bar at 273.15 K thus constitutes the shift \( \left( \mu_{298ºK}^* - \mu^* \right) \) resulting from the reversible mass transfer of 1 % w/w H from the sorbent into the zero-chemical potential of the gas phase:

\[
\mu_{298ºK}^* - \mu^* = R \cdot 273.15 K \cdot \ln \left( \frac{0.005 \text{ bar}}{1 \text{ bar}} \right) = -12033 \text{ J (mol H}_2\text{)}^{-1} \text{[1 % w/w H]}^{-1}_\text{max, rev} \tag{7}
\]

Taking up the thread how \( \mu_{298ºK}^* \) can linearly predict the maximum reversible hydrogen storage capacity as by equation 5, it has been shown for equation 6 that the pressure of 0.005 bar can be expressed as \( \Theta \cdot p^* \) with \( \Theta = 1.618 \) and \( X = -11 \). Thus, equations 5, 6 and 7 combine to equation 8, with \( (p) = (p/p^*) \).

\[
\frac{-\Delta H}{\mu_{298ºK}^*} = \frac{\mu_{298ºK}^*}{\mu_{0.005 \text{ bar}, 273 K}^*} \left[ \text{1 % w/w H]} \right]_{\text{max, rev}} \approx \frac{T \ln(p)}{T^* \ln(1.618) \left[ \text{1 % w/w H]} \right]_{\text{max, rev}}} | X = -11 \tag{8}
\]

It is discernible that equation 8 contains with \( T/T^* \) a Charles’ law proportionality term but it is more expedient to substitute \( T \) and \( T^* \) by their respective ideal gas law expressions \( T = pV_m/R \).

The negative arithmetic sign of \( X \) cancels out what moves the pressure gradient related to \( \mu_{298ºK}^* \) above 1 bar due to the symmetry of the \( \ln \)-function. With the logarithmic relation \( \log_a(x) / \log_a(y) = \log_a(y) \), equation 8 is transformed to equation 9.

\[
\frac{-\Delta H}{\mu_{298ºK}^*} \approx \frac{p^* V_m}{p \cdot (V_{0, m}) X} \left[ \text{1 % w/w H]} \right]_{\text{max, rev}} \]

\[
p^* = 1 \text{ bar}; \quad T^* = 273.15 \text{ K}; \quad V_{0, m} = 22.7 \text{ L}; \quad Y = \log_{1.618} \left( \frac{p}{p^*} \right); \quad X = 11 \tag{9}
\]

Equation 9 shows that the division of a negative equilibrium desorption enthalpy \( -\Delta H \) (respective a \( \mu_{298ºK}^* \)) by \( \mu_{298ºK}^* \) leads to an ideal gas \( pV_m \)-energy proportionality term which is multiplied with the quotient of the logarithms to the base of \( \Phi \). The resulting maximum reversible gravimetric storage capacity notes relative to 1 bar desorption pressure.

The corresponding maximum volumetric storage capacity is calculable via the density of the sorbent phase since equal to the quotient of volumetric and gravimetric hydrogen storage capacity. Since the predictions are bound to 1 bar reference pressure, but desorption at reduced pressure can pretense a higher reversible hydrogen storage capacity, conceptual emancipation from this intrinsic constraint is reasonable.

The molar Gibbs enthalpy of hydrogen gas at a distinct pressure and temperature is identical to the chemical potential \( \mu_{298ºK} \) and \text{HEMMES et al} calculated and tabulated these data for temperatures ranging from 100 K to 1000 K at pressures from 1 bar to 1 Mbar. Figure 2 shows the dependency of the isothermal molar Gibbs enthalpy of hydrogen between 100 K and 1000 K from pressure in 100 K increments. The array of curves fits to the general form shown in equation 10.

\[
G_{m, H_2}(T, p) = a(T) \cdot \ln(p) - b(T) \tag{10}
\]

The functions for the coefficients \( a(T) \) and \( b(T) \) can be determined graphically from the respective data set (Electronic Supplementary Information available). Coefficient \( a(T) \) shows a linear dependency to temperature, presented in equation 11a.

The temperature dependency of the coefficient \( b(T) \) fits best to a polynomial function of third order according to the formula shown as equation 11b, for the reason of clarity are the terms aligned as vertical sum.

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

![Figure 2. Semi-logarithmic plot of the isothermal pressure dependency of the molar Gibbs enthalpy of hydrogen based on the data of HEMMES et al for temperatures from 100 K to 1000 K in 100 K increments and pressures up to 1000 bar. The curves fit the general form shown in equation 10.](image-url)
Combining equation 10 with equations 11a and 11b leads to a numerical approximation for the molar Gibbs enthalpy of hydrogen as function of pressure and temperature alone, shown in equation 12. Equation 12 reproduces reasonably well the tabulated data of HEMMES et al.\textsuperscript{19} in the prime pressure and temperature domain \( p \leq 100 \) bar and \( T \geq 300 \) K of reversible metal hydride hydrogen sorption is the deviation below \( \pm 1.0 \) %.

\[
G_{m,H_2}(T,p) = \frac{8.363}{J \text{ mol} \text{ H}_2^{-1}} \frac{J}{K^{-1} \text{ mol} \text{ H}_2^{-1}} \frac{J}{T} \ln(p) \\
+ \frac{1.404}{10^2} \left( \frac{J}{\text{ mol} \text{ H}_2^{-1}} \right) \ln(p) \\
+ \frac{2.120}{10^3} \left( \frac{J}{\text{ mol} \text{ H}_2^{-1}} \right) K^3 T^3 \\
- \frac{6.519}{10^2} \left( \frac{J}{\text{ mol} \text{ H}_2^{-1}} \right) K^2 T^2 \\
- \frac{9.620}{10^3} \left( \frac{J}{\text{ mol} \text{ H}_2^{-1}} \right) K^1 T \\
+ \frac{3.065}{10^3} \left( \frac{J}{\text{ mol} \text{ H}_2^{-1}} \right) (11b)
\]

Division of equation 12 by \( \mu_{H_2}^{*\text{rev}} = -12033 \) \( J \text{ mol} \text{ H}_2^{-1} \) \( 1 \) \% w/w \( H_2 \) \( max, \text{rev} \) yields the ideal maximum reversible storage capacity of a hydrogen sorbent as function of pressure and temperature.

\[
(\Delta \text{ w/w H})_{max, \text{rev}}(T,p) = \frac{-6.950}{10^4} \left( \frac{1}{1 \text{ w/w H}} \right) \frac{K^3 T}{J} \ln(p) \\
+ \frac{-1.167}{10^2} \left( \frac{1}{1 \text{ w/w H}} \right) \frac{K^3 T}{J} \ln(p) \\
+ \frac{-1.762}{10^9} \left( \frac{1}{1 \text{ w/w H}} \right) \frac{K^3 T^3}{J} \ln(p) \\
+ \frac{5.418}{10^6} \left( \frac{1}{1 \text{ w/w H}} \right) \frac{K^3 T^2}{J} \ln(p) \\
+ \frac{7.995}{10^3} \left( \frac{1}{1 \text{ w/w H}} \right) \frac{K^3 T}{J} \ln(p) \\
\]

Equation 13 accounts for desorption at reduced pressure and it is discernible that a pressure below 1 bar will lead to a change in arithmetic sign of the \( \ln(p) \) term, resulting in a positive contribution to maximum reversible storage capacity, in line with experimental reality.

Plotting the temperature versus the pressure of equation 13 values unveils the contour lines of ideal constant maximum reversible hydrogen storage capacity, shown in Figure 3. Since the data of HEMMES et al. are the result of calculations accounting for hydrogen real gas behaviour, these contour lines mark out the definite thermodynamic boundaries to reversible hydrogen sorption.

1. The ideal gas approximation for hydrogen applies for describing the reversible transition between a \( \mu_{H_2} \) and \( \mu^* \). Substitution of \( \mu_{H_2} \) by calculated real gas \( G_m \) values adapts the formalism to real gas behaviour.\textsuperscript{19}

2. Evidently, the formalism does not predict the actual experimental reversible storage capacity of a hydrogen sorbent but tells which reversible hydrogen storage capacity is allowed by thermodynamics; either relative to \( p^* = 1 \) bar or at a given \( (T, p) \) – condition.

3. Chemical optimization of the reversible storage capacity relative to 1 bar pressure is possible but only within the boundaries of the generalized form.

The formalism bases on the premise of a two-phase reversible gas-sorbet system. Therefore, it explicitly does not apply to irreversible or metastable metal hydrides such as \( LiAlH_4 \) or \( AlH_3 \). While neat \( LiAlH_4 \) shows a negative desorption enthalpy and is thus an irreversible material, e.g. \( \alpha-AlH_3 \) is sometimes ranked among the reversible systems since showing an exothermic formation enthalpy of about \( \approx 10 \) \( kJ mol^{-1} \) corresponding to \( -6.0 \) to \( -7.6 \) \( kJ mol^{-1} \).\textsuperscript{20,21}

This formally suggests reversibility but due to this small hydrogen fixation potential, \( AlH_3 \) becomes thermodynamically stable only at substantially higher hydrogen pressures (about 7000 bar) or much lower temperatures.\textsuperscript{22} Interestingly enough, the tabulated data of HEMMES et al. indicate a change in arithmetic sign from negative to positive for the molar Gibbs enthalpy of hydrogen between 5000 bar and 10000 bar pressure at 300 K what signals that hydrogen loses its tendency to adopt the gaseous state.\textsuperscript{19}

For these reasons is \( AlH_3 \) a spurious counterexample since its full thermodynamic reversibility depends on conditions under which the prerequisite of a two-phase gas-sorbet system is not valid anymore. It is however noteworthy that Wang et al. recently found 0.25 % w/w H out of 10 % w/w H nominal hydrogen content to be reversible for nano-confined \( AlH_3 \).\textsuperscript{23}

Discussion

Figure 3 displays the thermodynamic constraints to reversible hydrogen storage capacity at any \( (T, p) \) – condition: for example, the reversible desorption of 10 % w/w H against 1 bar desorption pressure requires a temperature of 900 K and it is futile to expect this reversible storage capacity at a lower temperature at this pressure. For simplicity of terminology, the reasoning towards this point subsumes under the formalism and the following boundaries need explicit denotation:
which fall well into the margin of reversible <0.63 % w/w H maximum reversible storage capacity above 1 bar predicted by the formalism.

Metal hydrides that are capable of reversible hydrogen sorption but start from a metastable off-equilibrium condition will adopt equilibrium composition upon prolonged cycling. This stable cyclic capacity is assessable via the formalism what provides a thermodynamic explanation for partial reversibility.

Conclusions
Approaching reversible solid hydrogen storage from the gas phase end leads to the conclusion that there are clear and definite boundaries to the reversible storage capacity, demarcated by the general form of the formalism (Figure 3). This finding is not directly accessible by any sorbent material-based calculation or experiment; the thermodynamic constraints to reversible hydrogen sorption become noticeable either from a gas-phase centred vantage point or in the long-standing invisible barriers to experimental reality. While the value of sound experimental work is beyond question, this is one striking example how an exclusive focus on tangibles can lead to the opposite of what may be the appropriate conclusion. This work can equally benefit reversible metal hydride research and fuel cell energy system development since the definite achievable reversible storage targets are now easily calculable from e.g. the fuel cell operational temperature and hydrogen supply pressure.

Furthermore, the ideal gas law is a cornerstone in the scientific conception of the world. This fundamental ideal demonstration how to attribute a chemical potential change to a reversible transfer of mass between two phases with general validity may be of avail to a better understanding of other reversible energy storage systems. Thus, this work may prove of wider value and inspire solutions for problems to which the ideal gas law is reasonably applicable and equilibrium thermodynamics are of prime importance.

Acknowledgements
The partial funding of this work within the European Space Agency Contract No. 4000105330/12/NL/CLP and European Defence Agency Contract No. A-1341-RT-GP merits grateful acknowledgement. I would like to thank Dr. Christoph Buchner and Joachim Gerger for their assistance with the drawing of Figure 3 in Python.

Conflicts of interest
There are no conflicts to declare.

Notes and references
