

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

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Abstract

This article unveils on basis of the ideal gas law, the atomic conception of matter and classic equilibrium thermodynamics the ideal final regularity of reversible hydrogen mass transfer. This result allows to clarify problems of metal hydride chemistry which otherwise are impossible to understand e.g. why the substitution of 4 mol % Na by K in Ti-doped NaAlH_4 raises the reversible hydrogen capacity by 42 % at no substantial change to thermodynamic reaction parameters or how the dopants take effect in (Rb/K)-co-doped $\text{Mg(NH}_2\text{)}_2/2 \text{ LiH}$; both cases are discussed in this context. This ideal final regularity is a hitherto missed out superposition of physical chemistry fundamentals and defines the maximum specific energy at distinct conditions: directly for two-phase hydrogen storage methods and indirectly for electrochemical systems due to the normative role of hydrogen electrode potentials.

1. Introduction

Reversible metal hydrides for hydrogen storage^{1–4} are a means for reducing the pV -energy inside a pressurized gas storage container,^{5,6} and since consuming heat for hydrogen release,⁷ they can reduce the waste heat load of a fuel cell.⁸ They separate into irreversible and (partially) reversible metal hydrides depending on whether the heat tone of the hydrogenation reaction is negative (reversible) or positive (irreversible). However, despite the near-ideal properties of hydrogen and reversible chemical hydrogen storage essentially being a matter of classic equilibrium thermodynamics, explanations for partial reversibility on that basis are non-existent in the literature to date. That is insofar accountable as academic consensus opinion considers the issue first and foremost a matter of kinetic hindrance and thus, any metal hydride of a negative hydrogenation heat tone is supposed to be fully reversible in terms of sum formula. So why bother with a solution for an allegedly non-existing problem? There is either a long or a short answer and the latter it must be for the sake of brevity: Despite thousands of research papers over the last 50 years, the long-standing consensus view keeps failing to produce even hints of convergence in outcome in relation to its self-set hydrogen capacity targets (ultimately reversible 10 % w/w H on tank system (!) level $\cong \text{LiBH}_4$ of 18 % w/w H on material level at PEM-fuel cell conditions). Inconclusiveness is a bad sign in science to which convergence in outcome is indispensable; it might be a fine line between tenacity and delusion in R&D but after decades of stagnation, the presuppositions of the status quo (ante) merit questioning. Yet some remarkable experimental discoveries were made in the event but could not be adequately explained either; at large, the subject is in need of more sense, not more tangible data: there is already tons of it and in sum these point at some thermodynamic final regularity regarding specific hydrogen capacity.

Since hydrogen can under typical metal hydride sorption reaction conditions ($T > 300 \text{ K}$ and $p < 100 \text{ bar}$) be well-approximated as ideal and the issue relates to classic equilibrium thermodynamics, a fundamental ideal answer must exist. However, the empiric positivist bias ruling academic consensus opinion on the matter deems the existence of such an answer impossible (or at least insignificant) because the three main subaltern metal hydride classes, interstitial, complex and salt-like,^{1–4,9,10} show very different material features, in part even among their individual systems: So except for the evident shared feature of reversible hydrogen absorption, there is no discernible common ground as far as sorbent phase tangibles are concerned and for that reason the existence respective significance of a higher global regularity can be dismissed. While this argument shows some thought, it shows defective thought and even anticipates the prerequisite for the answer of opposite quality.

2. Methodical Approach

Said prerequisite is a switch of perspective from material-based tangibles towards gas phase thermodynamics for describing the condition of the storage system. This is viable in an equilibrium system and the thermodynamics of an ideal gas (hydrogen) are incomparably easier to handle than those of a solid that changes molar volume and all related properties during reaction. The classic van't Hoff equation by which the reaction parameters ΔH_m° and ΔS_m° of a reversible metal hydride can be determined is founded on that very principle: it relates the chemical potential of the ideal gas with the 2nd law of thermodynamics, equation 1 expresses it for desorption ($\Delta H_m^\circ > 0$).

$$\ln \left(\frac{p_{eq}}{p^\circ} \right) = \frac{-\Delta H_m^\circ}{R T} + \frac{\Delta S_m^\circ}{R} \quad (1)$$

Equation 1 tells the equilibrium pressure above the metal hydride as a function of temperature; the quantities ΔH_m° and ΔS_m° are obtained from a linear interpolation of distinct equilibrium pressures versus reciprocal temperature towards $p^\circ = 1$ bar, the intrinsic reference of the ideal gas chemical potential. For that reason, the quotient $\Delta H_m^\circ / \Delta S_m^\circ$ gives the temperature T_{1bar} which is virtually a metal hydride-specific constant (experimental factors aside). The basic relation of the van't Hoff equation is re-phrased in equation 2, placing thermodynamic standard pressure p° in the numerator of the ln-term.

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

Equation 2 shows thus with $(\mu^\circ - \mu)$ the negative definition of an ideal gas chemical potential $-\mu_{H_2}$ and equation 3 follows accordingly.

$$\ln \left(\frac{p^\circ}{p_{eq}} \right) = \frac{\Delta H_m^\circ}{R T} - \frac{\Delta S_m^\circ}{R} = \frac{-\mu_{H_2}}{R T} \quad (3)$$

Forming the derivative of equation 3 with respect to temperature reveals that ΔH_m° of the sorbent ($\Delta H_m^\circ > 0$) is equal to $-\mu_{H_2}$ in the reversible transition of pressure p_{eq} towards p° as shown in equation 4.

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

Equation 4 tells that placing a discharged reversible hydrogen sorbent into a hydrogen gas phase at $p^\circ = 1$ bar results in an excursion of the gas phase chemical potential from μ° by $-\mu_{H_2}$ equal to the reaction enthalpy ΔH_m° . Re-establishing a pressure of 1 bar above the sorbent requires the temperature $T_{1\text{bar}} = \Delta H_m^\circ / \Delta S_m^\circ$. Hence the van't Hoff equation asserts by principle all possible reversible hydrogen sorbents in terms of their featured chemical potential excursion from μ° . This leads further to the realization that this van't Hoff ΔH_m° scale can tell about the maximum reversible hydrogen mass transfer in [Δ % w/w H] if calibrated to a reference ideal gas chemical potential $\mu_{1\%H}^\circ$ bearing first-increment quality of 1 % w/w H mass transfer at IUPAC Standard Temperature and Pressure (STP). Equation 5 shows that hypothesis relating ΔH_m° respective $-\mu_{H_2}$ and $\mu_{1\%H}^\circ$ to reversible hydrogen mass transfer.

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

The linear-logarithmic proportionality question of equation 5 may be approached via the fundamental relation for changing the logarithmic base $\log_a(x)/\log_a(y) = \log_y(x)$. For example, in the chemical potential of an ideal gas at $T^\circ = 273.15$ K and 0.005 bar the pressure of 0.005 bar may be seen as $0.005 p^\circ$. Expressing 0.005 in exponential form to a different base e.g. the golden ratio $\Phi \approx 1.618$, thus 1.618^X with $X = -11.011$ eliminates standard pressure as factor inside the ln-term as is shown in equation 6.

$$\mu_{(0.005 \text{ bar}, T^\circ)} = R T^\circ \ln \left(\frac{1.618^X p^\circ}{p^\circ} \right) = X R T^\circ \ln (1.618) \quad | \quad X = -11.011 \quad (6)$$

So what happens if a van't Hoff ΔH_m° in the sense of equation 5 is divided by the exemplary chemical potential of equation 6? The answer is shown in equation 7.

$$\frac{\Delta H_m^\circ}{\mu_{(0.005 \text{ bar}, T^\circ)}} [1 \% \text{ w/w H}] = \frac{-\mu_{H_2}}{\mu_{(0.005 \text{ bar}, T^\circ)}} [1 \% \text{ w/w H}] = -\frac{R T \ln (p/p^\circ)}{R T^\circ X \ln (1.618)} [1 \% \text{ w/w H}] \quad | \quad X = -11.011 \quad (7)$$

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 universal gas constants cancel out (as does by principle the negative arithmetic sign of X with those in the numerator) which equation 8 shows accordingly:

$$\frac{\Delta H_m^\circ}{\mu_{(0.005 \text{ bar}, T^\circ)}} [1 \% \text{ w/w H}] = \frac{-\mu_{H_2}}{\mu_{(0.005 \text{ bar}, T^\circ)}} [1 \% \text{ w/w H}] = -\frac{p V_m}{p^\circ V_m^\circ} \frac{Y}{X} [1 \% \text{ w/w H}] \quad (8)$$

$$p^\circ = 1 \text{ bar} \quad T^\circ = 273.15 \text{ K} \quad V_m^\circ = 22.71 \text{ L} \quad Y = \log_{1.618} \left(\frac{p}{p^\circ} \right) \quad X = -11.011$$

Equation 8 shows that a division operation in the kind of equation 5 results in direct proportionality indeed, resulting in an ideal gas pV_m -energy proportionality term multiplied with the quotient (Y/X) comprising of the logarithms to a certain base, here e.g. Φ . With that point settled, the definition ideal gas chemical potential $\mu_{1\%H}^\circ$ may be approached and two of its three variables are already set for IUPAC Standard Temperature and Pressure (STP) condition applies: temperature is $T^\circ = 273.15 \text{ K}$ and one end of the pressure gradient is fix at $p^\circ = 1 \text{ bar}$. Thus, the tricky task is defining the other pressure for the quality of first-increment $[1 \% \text{ w/w H}]$ mass transfer.

3. Results

Thermodynamics are by their very nature a relative affair, structured to a defined standard state. However, the issue at hand demands to mark out an absolute origin which may not seem feasible within that base conception. But what actually defines that absolute zero reference point in this mass transfer context? It is given by the maximum off-equilibrium condition from the standard chemical potential at STP and that is something well-imaginable because 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 hypothetic zero-pressure vacuum. Since the reference state is given by STP at which the ideal gas adopts a molar volume of 22.71 L, this is the set free volume surrounding the sorbent. 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 therefore result in a system pressure of 0.005 bar.

That is the sought pressure constituting $\mu_{1\%H}^\circ$: knowledge of that hypothetical absolute zero-origin from μ° at STP is non-essential because only the pressure information after the fact of 1 % w/w H mass transfer is vital. But is $\mu_{1\%H}^\circ$ really a quantity of general validity? Yes because of its intrinsic reference to the mass of the hydrogen atom which happens to be virtually the base relative mass unit by which the atomic masses of all other elements of the periodic table scale. Equation 9 gives the value of this ideal reversible 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 develop equation 9 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.¹¹ Figure 1 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.

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

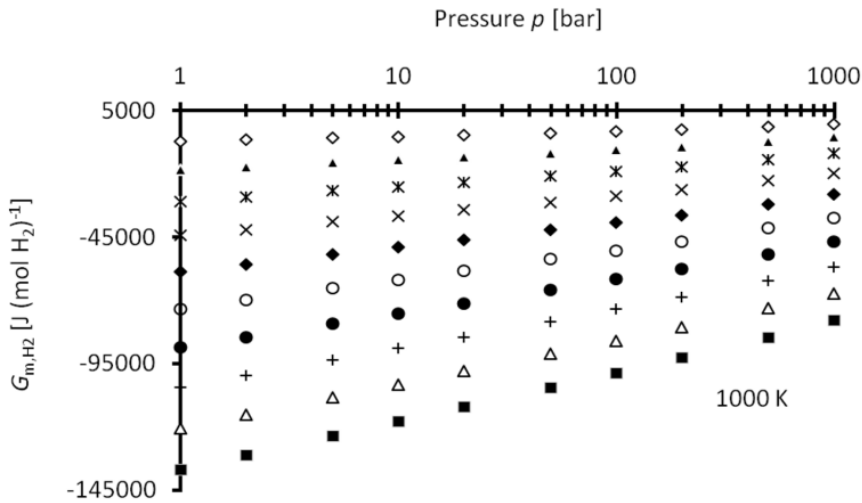


Figure 1 Semi-logarithmic plotting of the isothermal pressure dependency of the molar Gibbs enthalpy of hydrogen in 100 K increments on basis of the data of HEMMES *et al.*¹¹

The solutions for the coefficients $a(T)$ and $b(T)$ are graphically determined (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 sake of clarity.

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

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

Equation 10 is now augmented by equations 11a and 11b, yielding 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 $\pm 1.0\%$.

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

Division of equation 12 by $-12033 \text{ J (mol } H_2)^{-1} [1 \% \text{ w/w H}]^{-1} = \mu_{1\%H}^\circ$ yields the ideal maximum equilibrium hydrogen mass transfer in relation to pressure and temperature as shown in equation 13.

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

It is discernible in equation 13 that a pressure below 1 bar causes the \ln -term to change arithmetic sign, resulting in a positive contribution to the maximum reversible hydrogen capacity, as experimental reality requires. Based on equation 13, a map of ideal maximum reversible hydrogen mass transfer can be created by plotting its values in a temperature-pressure diagram as displayed in figure 2, showing the contour lines of constant capacity for e.g. integer values (available as electronic supplementary information).

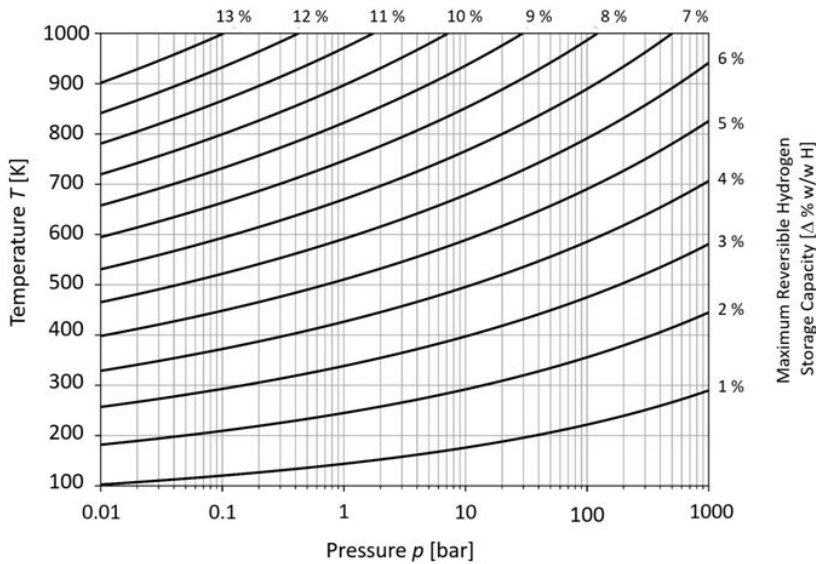


Figure 2 Semi-logarithmic plotting of equation 13 values in a temperature versus pressure diagram, showing the contour lines of constant maximum hydrogen capacity.

4. Discussion

Figure 2 shows the equilibrium hydrogen storage capacity being a function of the chemical potential of the gas phase respective pressure and temperature. This translates further to the van't Hoff ΔH_m° scale and a sorbent's thermodynamics may be generally understood in terms of a reflection of those of the gas phase. The bridge between free enthalpy and reversible mass transfer is the ideal constant of reversible hydrogen mass transfer $\mu_{1\%H}^\circ$ and the principle works both ways for the underlying equilibrium conception: a ΔH_m° enthalpy change in the sorbent phase translates to a change in hydrogen capacity and vice versa. Hence any sorbent property affecting hydrogen capacity (e.g. particle size) can be quantified in enthalpy terms without need for complex calculations. Consequently, two seemingly different sorbents of similar reversible specific hydrogen capacity should require similar release conditions and indeed such couples exist e.g. VH_x /Ti-NaAlH₄ or MgH₂/N-ethyl carbazole.

This can be further abstracted to the conclusion of a continuum of two-phase hydrogen storage systems along the van't Hoff ΔH_m° scale, from liquid hydrogen (LH2) to the most stable reversible hydrogen-bearing compound, not necessarily a metal hydride. Regarding LH2, it may seem a conceptual issue that the gravimetric hydrogen storage capacity is always 100 % H but the value on the van't Hoff ΔH_m° scale can be calculated from the density of LH2 (70.08 g L⁻¹ at 20 K) by means of $[1\% \text{ w/w H}]^{-1} = [2 \text{ g H}_2 / 200 \text{ g}]^{-1} = [1 \text{ mol H}_2 / 200 \text{ g}]^{-1} = [22.71 \text{ L} / 200 \text{ g}]^{-1} = [0.11355 \text{ L} / 1 \text{ g}]^{-1} = 8.8067 \text{ g L}^{-1}$: Dividing LH2 density and multiplying with $\mu_{1\%H}^\circ$ yields $-95.8 \text{ kJ (mol H}_2\text{)}^{-1}$ for the value of this storage method on the ΔH_m° van't Hoff scale. This figures to an ideal 33.5 % abatement from the calorific oxidation value of $-286 \text{ kJ (mol H}_2\text{)}^{-1}$ for liquefaction, well-approximating industrial process efficiencies.¹²

This displays the result's practical relevance despite its ideal-theoretical origin and elucidating the causality of doping effects becomes viable, too. This is a subject otherwise near-impossible to make sense of in consistent manner: in two particular cases doping proved remarkably successful, (4 mol % RbH / 4 mol % KH)-co-doped Mg(NH₂)₂ / 2 LiH and (4 mol % Ti / 4 mol % KH)-co-doped NaAlH₄,^{13,14} but explaining the why and how did never advance much beyond the obvious in the literature to date; a discussion of both systems in relation to this work's findings is available as electronic supplementary information.

It seems strange that this vital ideal thermodynamic final regularity of reversible hydrogen mass transfer evidently eluded recognition throughout the 20th century to the present day. It cannot be for a lack in knowledge or data so the reason must relate to the intangible sphere of the human mind, how science as a human activity is perceived and the data it produces are processed. Discussing matters touching philosophy may seem indecent in a paper of scientific scope but dropping this point is not well-possible either as touching the vital question of whether the results of this paper are admissible and can convey truth in a scientific sense, regardless of fact.

This work's line of argument bases on abstractions from measurements; long-standing, fundamental ones but abstractions nonetheless so its results cannot rise in self-evidence from any individual measurement. On these grounds it may be claimed from the empiric positivist bias that this were no science because unrelated to tangible experiment or that no new insight was conveyed. Yet the ideal gas law itself does not abide well by this standard either: imaging the unknown empiric positivist reviewer's response if Clapeyron tried to publish the ideal gas law not in 1834 but nowadays is as revealing as fun, the reproaches of cherry-picking and no new insight would surely be found in it. The same applies to the laws of thermodynamics of which only the first might be seen founded on the measurement of tangibles (already debatable), the other ones represent subsequent deductions from it.

The utilitarian, decadent element to empiric positivism and why it advanced to academic consensus attitude in the event of the 20th century merits exposition in a dedicated effort, its inadequacy as an objective truth-seeking

philosophy of science is blatant though: The objective study of the nature of a material item is supposedly only possible by means of tangibles obtained from methods based on the laws of causality to matter (virtually ignoring how these were identified); yet at the same time the possible significance or even existence of any higher, not directly measurable, regularity to which those basic laws may superimpose further is denied.

This is what this paper is all about: a hitherto missed out superposition of physical chemistry fundamentals to a thermodynamic ideal final regularity of reversible mass transfer. Figuratively speaking, it might be old cutlery but as far as hydrogen is concerned, it still cuts razor-sharp.

5. Conclusion

It follows from the ideal gas law, the atomic conception of matter respective the structure of the periodic table and classic equilibrium thermodynamics that there is an ideal final regularity of reversible hydrogen mass transfer. This sets the margin for the specific energy attainable in reversible chemical energy storage systems, directly for two-phase hydrogen storage methods and indirectly for electrochemical systems for the normative role of hydrogen electrodes. This result is not accessible from an exclusive bias on sorbent material properties but requires emphasis of the gas phase as connecting principle between all two-phase hydrogen storage materials.

6. Acknowledgements

This work spun-off from those done under European Space Agency grant 4000105330/12/NL/CLP and European Defence Agency grant A-1341-RT-GP at FOTEC Forschungs- und Technologietransfer GmbH, Austria which merits grateful acknowledgement. I would like to thank my former colleagues Dr. Christoph Buchner and Joachim Gerger for assistance with drawing figure 2 in Python.

7. Conflicts of interest

There are no conflicts to declare.

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