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Introduction

1.1 Motivation and aims of the work

1.1.1 The hydrogen energy transition

The worldwide effort to limit the increase in global average temperature to well below 2 °C above pre-industrial levels [1] requires the development of a climate-neutral economy. To address this challenge, the European Green Deal has set ambitious targets: reducing greenhouse gas emissions by at least 55 % by 2030 and transforming Europe into the first climate neutral continent by 2050 [2]. Achieving these goals will require a fundamental transformation of energy production systems to reduce emissions.

A key component of this transition is the establishment of an energy production chain based on emission-free technologies. However, a significant challenge lies in the intermittent nature of current renewable energy sources, such as solar and wind. These sources are variable, producing excess energy under favorable conditions but insufficient energy when conditions are poor. This variability makes managing wasted energy an important task in the pursuit of a sustainable energy system.

In this context, hydrogen production powered by renewable energy, so-called "green hydrogen" offers a promising solution. Green hydrogen acts as an energy vector, capturing surplus energy during periods of high renewable production. This stored energy can then be used when renewable energy generation is low, helping to balance energy supply and demand. Thus, green hydrogen can play a vital role in the transition to a sustainable energy system [3].

Green hydrogen is particularly attractive because it is a renewable energy carrier that releases only water as a by-product when used [4, 5], closing its life cycle in a sustainable manner. This makes it an ideal candidate for reducing emissions across high-impact sectors, including transportation, industrial heating, chemical production, and steel manufacturing [6]. However, in order to fully integrate hydrogen into these sectors, advanced and reliable methods for hydrogen storage and delivery are essential.

Among the strategies being explored, stationary hydrogen storage systems

have gained significant attention. Acting as a buffer, these systems enable better control of energy production by storing the excess during periods of high renewable generation and releasing it when needed. This capability promotes a more efficient and resilient renewable energy infrastructure.

However, hydrogen storage presents its own challenges, as advanced technologies are required to ensure safe, efficient, and cost-effective storage. This need for improvement justifies the importance of ongoing research and technological development in hydrogen storage solutions to fully realize the potential of hydrogen as a reliable energy carrier in the transition to a climate-neutral economy. In the following sections, various hydrogen storage methods will be presented, along with a brief analysis of their advantages and drawbacks, highlighting the importance of a deeper phenomenological understanding of hydrogen's interaction with materials.

1.1.2 Hydrogen storage in molecular state

At first sight, the use of hydrogen as a fuel may appear to be an attractive strategy, as its elemental form is the lightest among all elements in the periodic table, and the combustion of hydrogen gas has the highest specific energy density, reaching 120 MJ kg^{-1} under ambient conditions [7]. This specific energy density is more than double that of conventional fossil fuels; for example, methane, gasoline, and diesel have 55.6 , 46.4 , and 45.6 MJ kg^{-1} , respectively. However, under standard conditions, hydrogen is stable as a gas, resulting in a poor volumetric energy density of $0.003 \text{ kW h L}^{-1}$ [8], which represents just a small fraction of that of, for example, methane, propane, and gasoline, 4.2 , 7.1 , and 9.0 kW h L^{-1} [9, 10].

Until the current technological stage, hydrogen has been stored mainly in its molecular form, as a compressed gas [11] or as a condensed liquid [12]. However, storing hydrogen in its molecular form presents intrinsic energetic disadvantages. This is because, to reach a volumetric energy density that is adequate, these molecular storage methods require additional work and heat to compress or liquefy the gas, which ultimately decreases the efficiency of using hydrogen as an energy carrier.

Figure 1.1 shows the comparison between the volumetric density of hydrogen in its molecular state as a function of pressure.

In theory, compressing hydrogen gas to 700 bar requires about 13% to 18% of its lower heating value (LHV) [14], while the work for liquefaction corresponds roughly to 10% of the calorific content of hydrogen. In practice, however, efficiencies for liquefaction approach 30%, elevating the energy required for these processes to increase to about 20% to 30% of the energy content of hydrogen [14, 15].

Further complications arise from a technological perspective. For example, gas cylinders are too heavy, and compressed hydrogen is therefore usually stored in lightweight carbon-fiber-reinforced composite tanks. These tanks, although lighter, are expensive due to their difficult manufacturing process, which imposes further complications for recycling. Moreover, even though

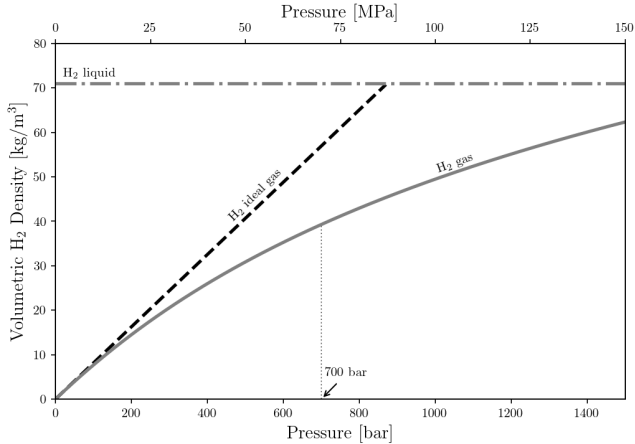


FIGURE 1.1: Comparison of volumetric hydrogen densities of liquefied, ideal and real gaseous hydrogen. The real hydrogen gas is plotted using Joubert's model [13] at 298.15 K.

they are stored in lightweight tanks, the energy density of hydrogen at 7×10^7 Pa (700 bar) is 5.6 MJ L^{-1} , which is six times lower than that of the commonly used gasoline, which has a density of 32.0 MJ L^{-1} .

In the same direction, hydrogen gas liquefaction requires a theoretical power input of 29.2 kJ mol^{-1} , and since this involves additional mechanical work, the equivalent heat can be expected to be around 2.5 times higher. The heat of combustion of H_2 to liquid H_2O has a value of $285.93 \text{ kJ mol}^{-1}$. In comparison, liquefying hydrogen gas represents 25 % of ideal efficiency [16].

Moreover, keeping the temperatures low necessitates additional components, which decrease the overall equipment volumetric and gravimetric storage capabilities. A further hurdle to molecular storage is the control of the boil-off. This phenomenon implies an estimated cost of 1 to 2 % daily hydrogen loss from the tank in mobile applications [7], which also creates problems in terms of fuel refueling frequency, cost, and safety [14].

1.1.3 Hydrogen storage as metal-hydrides

The possibility of storing a high volume of hydrogen in metals has been the subject of study since 1866, when Thomas Graham reported that palladium could massively absorb (at that time referred to as "occlude") 935 times its own volume of H_2 [17]. However, only in the 1960s, after almost a century, did metals begin to be investigated for hydrogen storage purposes [18]. Metal hydrides as solid-state hydrogen storage materials have several ad-

vantages over other classes of hydrogen storage media, owing to their high volumetric capacity and great hydrogen retention characteristics, allowing for nearly loss-free hydrogen storage during dormancy [19, 20]. In addition, metal hydrides are often considered safer storage solutions for applications where safety is a concern, since their (de)hydrogenation cycles can operate under mild conditions compared to compressed gas-based storage, which requires extremely high pressures [21, 22]. Their exceptional properties are a manifestation of the thermodynamics of the phase transformations governing the hydrogenation of these materials in the presence of hydrogen activity, which are explored in the following sections.

Fundamentals of the thermodynamics of *binary* metal-hydrides

Hydrogen reacts with many different elements to form various compounds and is usually classified by chemical bond type. Metallic hydrides, by the nature of metallic bonding, commonly exist over extended ranges of nonstoichiometric compositions and can be called interstitial alloys since hydrogen usually occupies interstitial sites of the metallic lattice [23].

The absorption of hydrogen in metals generally proceeds through several stages. First, physisorption occurs, where hydrogen is stabilized on the metal's surface by van der Waals forces. Next, in chemisorption, molecular hydrogen dissociates into atomic hydrogen (H) on the surface of the host material, forming metal-hydrogen chemical bonds. Following this, hydrogen atoms diffuse into the metal's bulk and generate a solid solution of hydrogen within the interstitial sites of the metallic lattice [24].

As the partial pressure of hydrogen increases, the solid solution can transition into a hydride phase, commonly referred to as the α - to β -phase transformation. This transformation continues until the α phase is fully converted to the β phase, provided that external thermodynamic conditions favor the stability of the hydride phase (β) over the solid solution phase (α).

In some materials, the metallic structures of the hydrogen solid solution and the hydride are quite similar. At higher temperatures, even under high pressure, hydrogen atoms tend to be randomly distributed within the lattice, making phase boundaries indistinct. However, at lower temperatures, hydrogen atoms may adopt a more ordered distribution within interstitial sites. This arrangement of hydrogen distribution can be interpreted as a spinodal decomposition if the crystal structure is significantly similar, as well as the formation of a completely new phase, depending on how substantial the changes in the crystal structure are for establishing distinct phase boundaries. The origin of phase separation arises from the interactions among dissolved hydrogen atoms, which incorporates both elastic and electronic contributions.

The structural changes associated with the transition from solid solution to hydride, particularly at low temperatures, can give rise to unique material properties. Often, after the completion of hydride formation, the hydride

itself undergoes additional structural adjustments to accommodate a larger number of hydrogen atoms within its interstitial sites.

Because of these combined structural and thermodynamic effects, the storage of hydrogen as a metal hydride offers several technical advantages. First, the volumetric hydrogen density can reach higher values in the hydride form because hydrogen atoms are more densely packed within the metal-hydride lattice compared to the liquid or compressed gas states. Second, metal hydrides can enhance safety since their decomposition is typically an endothermic process, requiring a change in external conditions and additional input energy to release hydrogen. This energetic input requirement reduces the risk of explosive reactions, providing an inherent safety mechanism.

Yet, the stability of the hydride should be considered for technical applications. If the forming compound with hydrogen is too stable or too unstable, it may not be worth reversing the reactions, as it then requires higher energy levels and other technical complications to make the process cyclic [16]. Investigating the stability of hydrides is therefore a necessary step when assessing the potential applications of metal hydrides. Their stability analysis involves understanding the thermodynamics of the hydrogenation process, which is generally characterized by evaluating their pressure-composition isotherm (PCI) curves [24].

In an ideal scenario for a *binary* metal-hydrogen system, the complete equilibrium between the bulk α , β solid phases and the hydrogen gas occurs in a defined pair of pressure (P) and temperature (T), at which all phases should present equal values of thermodynamic potentials. At this condition, the material system presents a flat plateau in the PCI curve. With increasing temperature, the pressure at which the plateau occurs increases, while the composition range of the plateau shrinks. Above a certain critical temperature (T_c), the plateau vanishes and the α - β transformation becomes a second-order thermodynamic transition, and the formation of the hydride becomes a continuous structural transformation upon pressure increase, from which phase separation is diffuse and unclear.

Below T_c , the hydride phase, or β -phase, is clearly distinct from the solid solution and grows when the hydrogen chemical potential, or hydrogen partial pressure, surpasses that of the plateau at a constant temperature. The formation of the hydride in this case involves nucleation and growth from the hydrogen supersaturation within the interstitial sites of the α phase.

The schematic representation of the properties of PCI curves over temperature and their associated description of a van't Hoff plot, together with a schematic illustration of the α - β structural transformation, is shown in Figure 1.2.

In general terms, the formation of the hydride can be seen as being controlled by concurrent thermodynamic factors, namely the enthalpy (ΔH_r) and the entropy (ΔS_r) of the reaction. These thermodynamic parameters characterize the variation in enthalpy and entropy of the hydride in relation to the metal plus the hydrogen gas states.

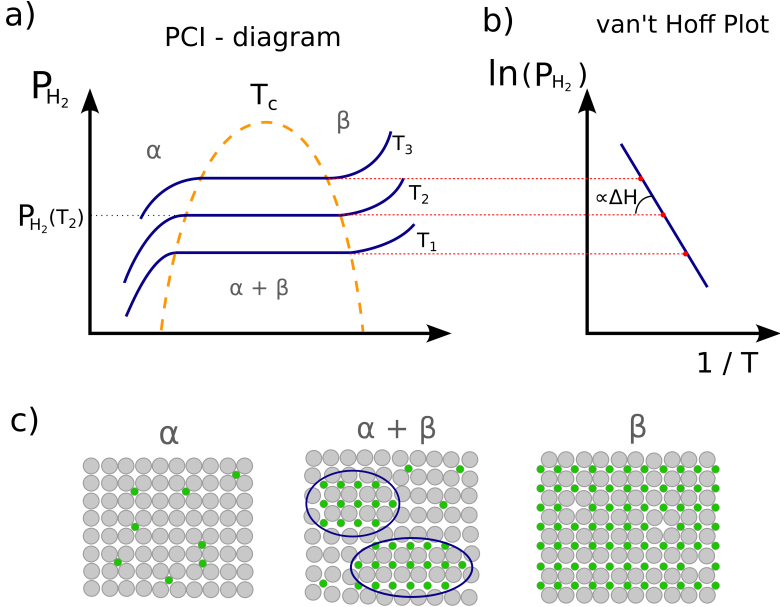


FIGURE 1.2: Schematic diagram of structural and thermodynamics of hydride formation. a) General behavior of PCI curves over temperature, with $T_1 < T_2 < T_3$. b) The associated van't Hoff Plot of curves shown in (a); c) Schematic illustration of the structural transformation of α - β transformation. The schematic diagram is an adaptation from the work of M. Dornheim [24].

As the main contribution to the entropy of the reaction comes from the change in entropy between hydrogen in gas form and its crystalline state within the interstitial site of the crystal, the reaction enthalpy can be considered the primary engineering parameter for materials design, which is introduced in the next subsection 1.1.3.

From the assumption of the equilibrium condition, i.e., the same hydrogen chemical potential (μ_H), the enthalpy and entropy over the constant pressure region of the phase diagram can be described by applying the isothermal Gibbs energy to the van't Hoff equation to derive its linear form (Equation 1.1) [24]:

$$\frac{1}{2} \ln \left(\frac{P_{eq}}{P_0} \right) = \frac{\Delta H_r}{RT} - \frac{\Delta S_r}{R}, \quad (1.1)$$

where P_{eq} represents the equilibrium or plateau pressure; P_0 is the standard pressure (101 325 Pa), and T is the varying temperature. Consequently, values of ΔH_r and ΔS_r are obtained, respectively, by the slope and the y -intercept, as shown in Figure 1.2b).

The thermodynamics of hydrogen adsorption/desorption govern their temperature and pressure range of applicability and can be analyzed through Equation 1.1 by performing a linear regression on the plot of the logarithm of the plateau pressure as a function of the inverse of isotherm temperatures (illustrated in Figure 1.2b)).

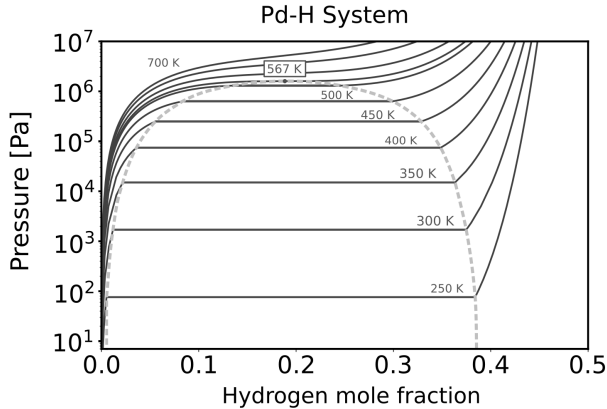


FIGURE 1.3: Calculated PCI curves for the Pd-H system over different temperatures. The plot shows the variation of plateau range for first-order phase transition up to its critical temperature. The PCI curves were calculated for 250 K to 700 K with steps of 50 K, including the calculation at the critical temperature 567 K. The calculations are performed with CALPHAD model provided by Joubert and Thiébaud [25].

The palladium-hydrogen system is a typical example used to discuss the thermodynamic properties introduced here. The hydride formed from the palladium metal has the same basic structure as the metal. The volume change of the solid-solution α -phase is negligible. In contrast, the β -phase has a volumetric expansion of approximately 11 % relative to the pure metal. At lower temperatures (below $T_c = 566$ K) the α - β transformation is a first-order thermodynamic transition, and the plateau pressure of the PCI is clearly defined. Figure 1.3 illustrates the calculated PCI curves for the Pd-H system based on the model of Joubert and Thiébaud [25], which is adjusted to experimental data.

The plateau pressure represented in red in Figure 1.3 is an invariant of the pressure-composition phase diagrams for a constant temperature. They represent the unique set of thermodynamic potentials that equalize the hydrogen

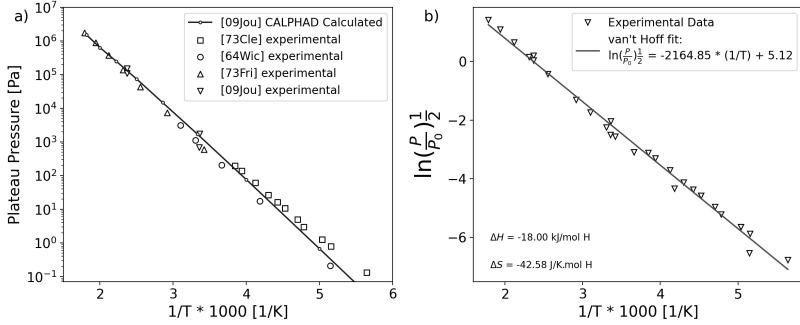


FIGURE 1.4: Equilibrium pressure over temperature. a) Calculated and experimental data of PCI curves of the Pd-H system with superimposed experimental data. The calculations are performed with CALPHAD model provided by Joubert and Thiébaud [25], and experimental data from 73Cle [26], 64Wic [27], 73Fri [28], and 09Jou [25]. b) Linear regression of the van't Hoff equation for the same experimental data from a).

chemical potential of the hydrogen solid-solution (α -phase), the hydride (β -phase), and the H_2 gas. By fixing these conditions within the thermodynamic model, i.e., requiring that these phases are in equilibrium, the temperature and pressure pair that satisfy such constraints can be calculated. The results of such calculations are shown in Figure 1.4a).

Note that by applying the proposed technique of the van't Hoff plot combined with the linear regression of the experimental data presented in Figure 1.4b), the values of reaction enthalpy and entropy can be determined. Using the CALPHAD model, these values are obtained by calculating the difference in enthalpy and entropy between the final and initial states of the system. From an experimental perspective, the thermodynamic aspects of metal hydride systems are straightforward but are sometimes limited to evaluating logarithmic plateau pressures against $1/T$. However, there are many other aspects of the thermodynamics of these systems.

Beyond the thermodynamics of bulk *binary* metal-metal hydride systems

One important aspect beyond the van't Hoff equation is the difference in experimental plateau pressure when measuring absorption or desorption curves, known as hysteresis. In fact, the equilibrium pressure-composition isotherm represents the state that would be observed if there were no boundaries between the solid-solution and the hydride phase. In reality, during absorption, the pressure must exceed that of the bulk equilibrium to begin transformation; during desorption, the pressure must drop below that to decompose

the hydride. The enthalpy derived from high-precision calorimetry measurements of binary hydrides confirms this. For example, the data measured for Pd-H have the same absolute value of ΔH_T for desorption and absorption [29], which confirms that the reversible α - β phase transition should be exact reverses of each other.

To understand the difference between PCI and calorimetric results, Flanagan and Oates [30] suggested that an ideal bulk thermodynamic equilibrium between the three phases should occur at a pressure level between the measured absorption and desorption plateau pressures. The conclusion is based on thermodynamic principles, as they demonstrated that these reactions would not generate entropy otherwise. In addition, they proposed that the evolved driving force, manifesting as heat from overcoming activation barriers, is partially the reason for the hysteresis.

An important aspect to note is that plateau pressures are invariant points (Gibbs phase rule) only in *binary* metal hydride systems; however, metal hydrides are often generated from intermetallic compounds or alloys. In substitutional alloys, for example, the Pd-Pt-H system, the complete equilibrium between the α , β , and gas phase implies a different metallic composition between the metallic solid solution and the hydride, and a "sloping plateau" is expected.

For metallic systems of higher than unary complexity, the thermodynamics of hydrogenation is often a phenomenon not in complete equilibrium. Instead, a paraequilibrium state governs the hydrogenation process. In this case, the metallic elements behave as a unique species due to their much lower mobility in comparison to the rapid diffusivity of hydrogen in the interstitial lattice and resemble a "frozen" metal situation. The system in this case can be referred to as pseudobinary hydrides. Under para-equilibrium conditions, only the chemical potential of the fast diffusing species, in this case hydrogen, is equal across all phases. The alloy composition, however, remains constant due to the slow mobility of metallic species, which maintain their chemical potential gradient through the different condensed phases [31, 30]. The concept of paraequilibrium will be explored further in Chapter 3 and Section 3.2.1.

Despite being different from what occurs in the bulk, in multicomponent metallic systems, even at paraequilibrium, a local equilibrium among the metals at the interface may exist. If this is the case, there is an induced compositional variation at the interface relative to the bulk, which may also influence the aspect of the PCI curve, e.g., inducing a sloped plateau [31, 30].

Furthermore, the variation of specific volume and composition between metal and hydride phases generates misfit strains and perturbed chemical bonds at the metal-hydride interface. Therefore, during the metal-metal hydride phase transformation, macroscopic energy barriers are induced, which have different natures during the hydrogenation and dehydrogenation processes. These differences partially explain the observed hysteresis [32, 33, 34].

These effects beyond bulk equilibrium have a substantial impact on hydrogenation properties. Since hydride formation often follows nucleation and

growth mechanisms, the characteristics of the interface between solid phases become critical. The interphase boundary energy includes a chemical component, arising from perturbed atomic bonds at the interface, which adds an energetic contribution to the system's total free energy. This chemical contribution scales with the area of the interphase boundary. Additionally, the lattice mismatch between the metallic and hydride phases introduces elastic strain energy within the boundary region, a mechanical contribution that scales with the volume of the forming phase.

The interplay between these chemical and mechanical contributions, along with bulk thermodynamic effects, is key to understanding hydrogenation mechanisms. In order to minimize the total free energy of the system, these contributions are balanced and dynamically adjusted against each other, thus driving the evolution of phase morphology and influencing the microstructure and kinetics of hydrogenation. These effects are further discussed in Chapter 4 and Chapter 5.

The interest of alloying and intermetallics as hydrogen storage media

Among metal hydrides, those based on binary intermetallic compounds with the general formula AB_n exhibit the thermodynamic and kinetic properties envisaged for hydrogen storage purposes. Elemental hydrides of early (A) and late (B) transition metals generally possess high negative and positive formation enthalpies (ΔH_f), meaning that they form very stable and very unstable hydrides under standard conditions, respectively [35]. In Figure 1.5, a periodic table of elements is illustrated that shows the data compiled from the formation enthalpy in Table 6.6.1 of Griessen and Riestere [36] and Table 1 from Griessen and Driessen [37] for most binary metal hydrides of interest. For some elements, where only the heat at infinite dilution ($\Delta \bar{H}_\infty$) was available, this value was used to estimate the formation enthalpy of the corresponding monohydride.

It is often observed that combining elements A and B in specific ratios (e.g. $n = 1, 2, 3, 5$) promotes the formation of stoichiometric intermetallic compounds, AB_n , which is accompanied by a reduction in the absolute value of the formation enthalpy, ΔH_f , of their corresponding ternary hydrides [38]. This reduction leads to the formation of ternary hydrides with intermediate stability, which enhances the reversibility of hydrogenation under conditions close to ambient temperature and pressure. This provides a safer hydrogen storage medium compared to molecular hydrogen tanks, which require either extremely high pressures or very low temperatures [35, 38].

Operating near ambient conditions is particularly advantageous when these materials are intended for use in residential or domestic areas. Furthermore, these intermetallics exhibit considerable variability in hydrogenation thermodynamics and kinetics when their base components are partially substituted with other suitable metals. This suggests a promising avenue for