

## HYDROGEN PRODUCTION AND SOLID-STATE STORAGE: A REVIEW

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### ABSTRACT

*This paper is a synthesis of the methods used for hydrogen production and the storage of hydrogen in the form of metal hydrides and different methods of hydrogen storage in various materials are presented. It also presents the Romanian vision in relation to the existing and future projects that include the production of hydrogen and its use in energy.*

KEYWORDS: hydrogen production, hydrogen storage materials, metal hydrides

### 1. Introduction

#### 1.1. General information about hydrogen

Hydrogen, with the symbol H and atomic number 1, has an atomic weight of 1.008, is the lightest element in the periodic table of elements. In monatomic form, it is the most widespread element in the universe, being found in a proportion of 75%. The most common isotope of hydrogen is protium (having the symbol <sup>1</sup>H), which is composed of a proton and devoid of neutrons [1].

**Table 1.** Physico-chemical properties of hydrogen [1]

Phase at STP*	Gas
Density	0.08988 g/L (0 °C, 1 bar)
Melting point	-259.14 °C
Boiling point	-252.87 °C
Molar heat capacity	(H <sup>2</sup> ) 28,836 j.mol <sup>-1</sup> K <sup>-1</sup>
Ionization potential	13.5984 eV
Specific heat	14,304 j/gK
Crystal structure	Hexagonal
Thermal conductivity	0.1805 Wm <sup>-1</sup> .k <sup>-1</sup>

\*Standard temperature and pressure

In nature, the most stable and common isotopes of hydrogen are:

1. Protium (0 neutrons, atomic number A = 1);

2. Deuterium (1 Neutron, atomic number A = 2);  
3. Tritium (2 neutrons, atomic number A = 3).

#### 1.2. Use of hydrogen

Hydrogen is one of the most viable energy sources for the future. It has a large energy storage capacity, and does not pollute if it is used as a fuel for transport, heating and electricity generation, in geographical areas where it is difficult to implement the infrastructure for electricity use [1].

Globally, this chemical element is considered to be the second source of energy, as an energy carrier. The energy carrier is used to transport, store and deliver energy in a form that is easy to use. Also, hydrogen is a contender for the future, in terms of energy, because a large volume of hydrogen can be easily stored in various forms. It is considered to be very efficient; its degree of pollution tends to zero and there is the possibility of being used in the field of transport, heat generation and electricity production [1].

### 2. Hydrogen production

Hydrogen can be obtained by the following methods:

1. extraction from hydrocarbons;
2. production from coal;
3. thermo-chemical processing of biomass;
4. electrolysis of water.

Through steam reforming, hydrogen will be extracted from hydrocarbons (natural gas) in two phases [2].

By adding steam at a temperature of around 500-800 °C and a pressure of 20-40 bar, the more complex hydrocarbons are broken down into methane, hydrogen, carbon monoxide as well as carbon dioxide to avoid clogging the catalyst in the reformer assembly. Methane will then react with the water in the presence of a nickel catalyst at a temperature of 700-1100 °C and a pressure of 25-30 bar, resulting in H<sub>2</sub> and CO [2].

The negative side of this process is that the secondary products, CO<sub>2</sub>, CO and other gases, because if are released into the atmosphere, it will have a strong greenhouse effect [2].

Biomass comprises of hydrocarbons and other waste streams, such as wastewater, which also contain organic substances from which hydrogen can be extracted. Hydrogen can be obtained from biomass by catalytic reforming with steam. Due to the fact that biomass contains up to 40% oxygen, it gasifies almost by itself [3].

There are different methods to produce hydrogen from water, such as: electrolysis of water, high-pressure electrolysis, high-temperature electrolysis, biocatalyzed electrolysis, radiolysis, thermolysis, and reaction with ferrosilicon [4]. A new method, developed in 2017 by researchers from the U.S. Army, can produce hydrogen by the interaction between water and powder based on nanogalvanic aluminium [5].

By the end of 2021, the origin of hydrogen production globally is: 47% natural gas, 27% coal, 22% petroleum, and 4% water electrolysis [6].

In Europe, hydrogen is currently used in less than 2% of energy consumption and is mostly used for the manufacturing of chemical products. A percentage of 96% of the hydrogen produced using natural gas, negatively affects the environment by producing significant amounts of CO<sub>2</sub> emissions [7].

In 2022, in Romania, steps were started to build several electrolysis plants, with a capacity of at least 100 MW each, which will be able to produce up to 10,000 tons of hydrogen, starting in 2025. The fields in the country that can use hydrogen as energy are industry, transport, district heating, but also energy storage after 2030 [8].

### 3. Hydrogen storage

Hydrogen can be stored in several ways, such as:

1. hydrogen as gas;
2. hydrogen storage in liquid form;
3. hydrogen storage in solid form.

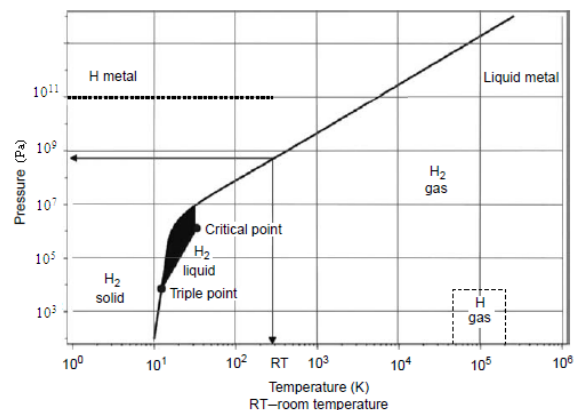
#### 3.1. Storage as gas in pressure vessels

One kilogram of hydrogen occupies a volume of 11 m<sup>3</sup> at normal pressure and temperature, and usually this type of storage requires high compression. Storing H<sub>2</sub> in gas form requires pressured vessels that withstand pressures between 3.5\*10<sup>6</sup> and 7\*10<sup>6</sup> Pa. High-strength steels or other metals are an option for hydrogen storage pressure vessels, but the diffusivity of hydrogen in the metal and the weight of the metal must also be considered. Other variants for the metals that can be used for the manufacturing of hydrogen pressure vessels are austenitic steels, but their high weight makes them impossible to be used for this purpose [9].

#### 3.2. Storage of hydrogen in liquid form

The energy density of hydrogen can be doubled compared to 68947.57 kPa of CH<sub>2</sub> for 70 g/L, by liquefaction at a temperature of 20 K, at atmospheric pressure. Five kg of hydrogen occupies a volume of only 71 L, which is equal to the volume currently occupied by the fossil fuel used in motor vehicles. The hydrogen phase diagram illustrates the appearance of different forms of hydrogen depending on temperature and pressure. There is a narrow segment where hydrogen can be found in liquid form with a density of 70.8 kg/m<sup>3</sup>, at a temperature of 20 K [9].

The energy required to obtain liquid H<sub>2</sub> represents approximately 30% of the lowest heating value of hydrogen. For these systems, there is a period when the hydrogen in the cylinders heats up and passes a gaseous phase, leading to the need to use ventilation systems of the liquid H<sub>2</sub> storage tanks [10].



**Fig. 1.** Phase diagram of hydrogen, adapted from Ref. [9]

In the specialized literature, an experiment was presented in which a mixture of H<sub>2</sub> (in a gas furnace), and liquid nitrogen, showed a fairly high density, at temperatures higher than the temperature at which hydrogen is liquid. Valorially, it was shown that a mixture with 70 mol% H<sub>2</sub> has a density of 45 kg H<sub>2</sub>/m<sup>3</sup>, at a temperature of 77 K and a pressure of 41.3\*10<sup>6</sup> Pa [11].

### 3.3. Storage in the form of metal hydrides

Metal hydrides are systems having the ability to store H<sub>2</sub>, at high temperatures and release it in the form of gas in order to be used as fuel. This reaction is carried out by heating metal hydrides at various high temperatures. Metal hydrides present an advantage, from the point of view of stored hydrogen, compared to storing H<sub>2</sub> in the form of gas or liquid, having a storage capacity of 0.13-0.15 kg H<sub>2</sub>/L. The simplest metallic and intermetallic alloys, such as

LaNi or FeTi, can react with hydrogen at low temperatures (100 °C) and low H<sub>2</sub> pressures. The mass percentage of H<sub>2</sub> in the case of these metal hydrides varies between 1.5% and 3%, and the hydrogen density per volume is between 0.05-0.12 kg H<sub>2</sub>/L [6]. Greater hydrogen storage capacities are found in materials such as Mg and MgNi, which form hydrides at temperatures of approximately 300 °C and H<sub>2</sub> pressures between 5\*10<sup>5</sup>-10<sup>6</sup> Pa. Although metal hydrides present advantages from the point of view of the high amount of H<sub>2</sub> stored in the volume unit, their problem is the relatively long time required to carry out the hydride-dihydride processes [9].

In 1998, in Augusta, Georgia, a bus that used hydrogen as fuel was implemented for the transportation of people. The hydrogen storage system consisted of a lanthanum-nickel-aluminium metal alloy, which can be hydrogenated at low temperatures and provides 6 kg of H<sub>2</sub>/h, ensuring the vehicle an autonomy of 300 km [12].

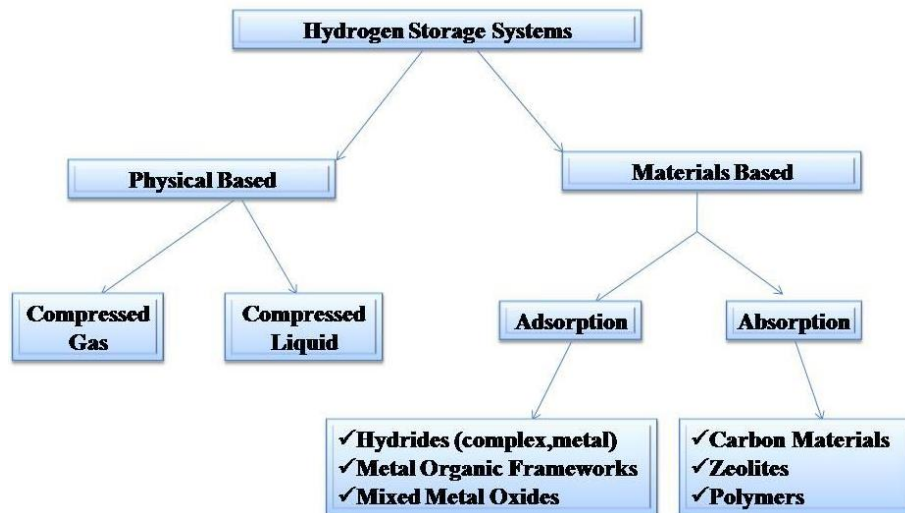


Fig. 2. Hydrogen storage systems, adapted from Ref. [10]

## 4. Storage of hydrogen in the form of hydrides

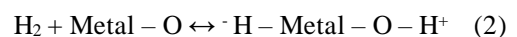
### 4.1. General information about hydrogen storage in materials

Chemical reactions of H<sub>2</sub> are of interest in fields such as chemistry or the use of hydrogen as a fuel. It is known that at a pressure of 10<sup>5</sup> Pa, H<sub>2</sub> passes from a gaseous state to a liquid state. If an electrical discharge is applied to hydrogen gas at low pressure, reactions such as molecular dissociation, ionization or recombination occur. These effects favour the formation of molecular hydrides, saline hydrides or metallic hydrides [13].

Molecular hydrogen can be separated by homolytic or heterolytic processes in contact with metals, metal oxides or a mixture of activated metal oxides. The homolytic dissociation results from the absorption of hydrogen by the substrates of the activated metal, according to the equation:



while the heterolytic dissociation reaction in H<sup>+</sup> and H<sup>-</sup> is found in the case of metal oxides [10], according to the equation:



Storing hydrogen in metals is one way that hydrogen can be released later to be used as fuel for combustion engines or batteries. Hydrogen can be stored in underground reserves, in large quantities, or in cylinders for storage in small quantities. The electrochemical storage of hydrogen in the form of batteries has the highest yield among all methods of storing this gas [14].

According to the Office of US Energy Efficiency and Renewable Energy, the technical requirements of a hydrogen storage system for vehicles are in Table 2.

**Table 2.** Requirements for hydrogen storage systems in the form of hydrides [15]

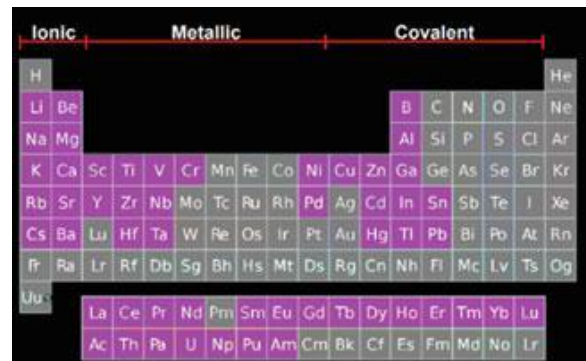
Storage parameter	Unit	2020	2025
Usable, specific energy from H <sub>2</sub>	kWh/kg	1.5	1.8
Usable energy density from H <sub>2</sub>	Kwh/L	1.0	1.3
Storage system cost	\$/kWh net	10	9
Operating ambient temperature	K	233/253	233/253
Min/max delivery temperature	K	233/358	233/358
Operational cycle life	Cycles	1500	1500
Min delivery pressure from the storage system	Pa	5*10 <sup>5</sup>	5*10 <sup>5</sup>
Max delivery pressure from the storage system	Pa	12*10 <sup>5</sup>	12*10 <sup>5</sup>
Onboard efficiency	%	90	90
System fill time	min	3-5	3-5
Average flow rate	(g/s)/kW	0.004	0.004

Hydrogen fuel cells work just like batteries, they generate electricity based on an electrochemical reaction. A fuel cell needs three primary elements:

hydrogen, oxygen and electrolyte. H<sub>2</sub> and O<sub>2</sub> chemically react forming water. In a fuel cell, there is no combustion process. The electrons released as a result of the chemical reaction produce an electric current through an external circuit [14].

#### 4.2. Types of hydrides

Hydride means a binary system, in which hydrogen forms compounds with other elements from the periodic table (E<sub>a</sub>-H<sub>b</sub>). Usually, hydrides fall into three major categories: ionic, covalent, and metallic.



**Fig. 3.** The ability of materials to form hydrides, adapted from Ref. [14]

1. In the case of ionic hydrides, hydrogen compounds together with the most electropositive metals (especially alkali and alkaline metals) form ionic hydrides by releasing H<sub>2</sub> in contact with Brønsted acids and transferring H<sup>-</sup> to electrophiles. This category of hydrides is also known as saline hydrides or pseudohalides. Ionic hydrides of the heaviest elements react violently with water and generate H<sub>2</sub> according to the reaction [14]:



2. Covalent (complex) hydrides, the hydrogen atom reacts with one or more nonmetals. Hydrogen forms covalent bonds with an electropositive element by giving up pairs of electrons. AlH<sub>3</sub>, BH<sub>3</sub>, BeH<sub>2</sub> are some examples of complex hydrides. However, BH<sub>3</sub> and AlH<sub>3</sub> are very unstable, because they form complex anion in combination with hydride anion. The most common situations are tetrahydridoborate (NaBH<sub>4</sub>) and lithium tetrahydridoaluminate (LiAlH<sub>4</sub>) [14].
3. Metal hydrides, also called interstitial hydrides, can be produced by the reaction of hydrogen with transition metals. Their specific

structure allows them to be non-stoichiometric, with variable composition. Using this idea as a basis, a crystalline network can be developed in which hydrogen atoms can fill the space in the structure and not in a well-defined order. The reaction of interstitial hydrides with H<sub>2</sub>O can produce H<sub>2</sub>, according to the following equation [14]:



## 5. Metal hydrides

Metal hydrides are found in solid form, are non-stoichiometric and have a good thermal conductivity. Metal hydrides, salts, intermediates and binary metal hydrides have been found, but there are also some elements, such as ruthenium, which do not form binary hydrides, but form complex metal hydrides. Since the 1970s, several alloys have been developed that have the ability to store hydrogen. These metal-hydrogen systems have the following general form: 1. AB<sub>5</sub>; 2. AB<sub>3</sub>; 3. A<sub>2</sub>B<sub>7</sub>; 4. AB<sub>2</sub>; 5. AB; 6. A<sub>2</sub>B; where A is the metallic element that absorbs hydrogen and B is an element with poor hydrogen absorption qualities, but with increased catalytic activity. The secondary element is very important in the hydrogen dissociation process.

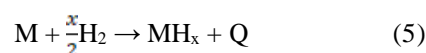
Metal-hydrogen bonds can be electrophilic or nucleophilic. The characteristics of the primary metal and the reaction conditions determine the properties of the metal hydrides obtained. Metal hydrides can be synthesized by metal protonation, oxidative addition of H<sub>2</sub>, the addition of nucleophilic main-group hydrides (borohydrides, aluminium hydrides and silanes) and elimination of β-hydrides. Metallurgical techniques are most often used to obtain metal

hydrides, and chemical processes are generally used to produce complex hydrides. The process of metallurgical hydride formation includes the activation of hydrogen absorption (through hydridation/dehydridation treatments) [14].

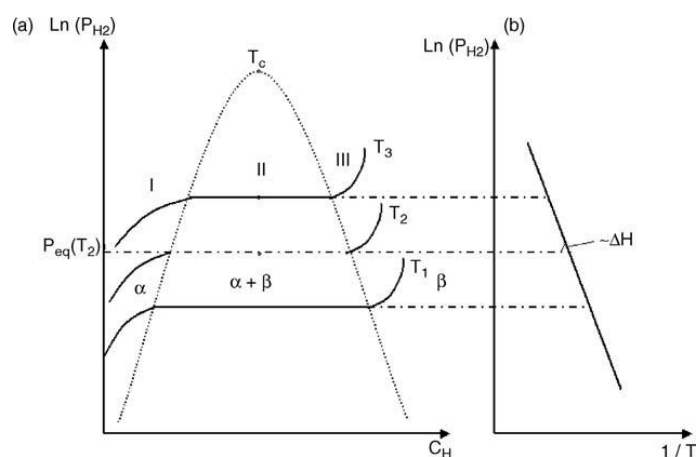
A wide range of metal alloys can be used as hydrogen storage systems. Some metal hydrides have a volumetric density, which is about 115 kg/m<sup>3</sup> (characteristic value of LaNi<sub>5</sub>), but the disadvantage of such systems is the high reaction temperature. Although hydrogen is absorbed under certain conditions (temperature, H<sub>2</sub> pressure, etc.) by some metals and metal alloys, this gas can be released from the metal hydrides obtained, and the metal or alloy from which the hydrogen was extracted is also recovered. Metal hydrides show a favourable character regarding hydrogen storage. Metal-H systems with light elements (such as Li, Be, Na, B and Al) are reliable materials in the field of hydrogen storage, especially considering that the H: Metal ratio is greater than or equal to 2 [14].

### 5.1. Thermodynamic properties of metal hydrides

Most metal hydrides are formed by exposing metals/metal alloys to hydrogen gas at certain temperatures and pressures. As previously presented, the formation reaction of metal hydrides is:



where Q is the heat released during the hydrogenation reaction. The thermodynamic properties of the reaction are described by pressure-composition isotherms (PCIs) [16].



**Fig. 4.** (a) Schematic representation of the pressure-composition isotherm, where  $\alpha$  is the solid solution of H<sub>2</sub> and  $\beta$  is the hydride phase [16]; (b) Van 't Hoff plot giving the enthalpy of hydride formation  $\Delta H$  [16]

At low concentrations (below 1), hydrogen dissolves in the metal structure and forms a solid phase solution ( $\alpha$ ). After that, the hydrogen is randomly distributed in the metal and its concentration varies slightly depending on the temperature. The  $\alpha$  phase has the same structure as the base metal. The thermodynamic equilibrium condition is given by the formula:

$$\frac{1}{2}\mu_{H_2}(p, T) = \mu_H(p, T, c_H) \quad (6)$$

where  $\mu_{H_2}$  is the chemical potential of molecular hydrogen,  $\mu_H$  is the chemical potential of atomic hydrogen in the metal and  $c_H$  is the hydrogen concentration (H/Metal ratio), being expressed as the number of hydrogen atoms per number of metal atoms [16].

As  $H_2$  pressure increases, the concentration increases until the H-H interaction becomes important. At this moment, a phase with a high concentration ( $\beta$  phase) appears in  $H_2$ . The system now has 3 types of phases ( $\alpha$ ,  $\beta$  and hydrogen in gas form) and two components (metal and hydrogen). From the Gibbs phase law, the degree of release is:

$$f = C - P + 2 \quad (7)$$

where C is the number of system components and P is the number of phases. It can be concluded that, in a two-phase region, the concentration increases while the hydrogen pressure is constant. When phase  $\alpha$  disappears completely and phase  $\beta$  is found exclusively in the system, the system has two degrees of release. Hydrogen penetrates the solid material, in the  $\beta$  phase, and its pressure increases with the concentration [16].

### 5.1.1. Thermodynamics at low concentration

At low pressures ( $P < 10^7$  Pa), hydrogen has the properties of an ideal gas and its chemical potential is given by the relation [16]:

$$\frac{1}{2}\mu_{H_2} = \frac{1}{2}H_{H_2}^0 - \frac{1}{2}TS_{H_2}^0 + RT\ln p_{H_2}^{1/2} \quad (8)$$

where  $H_{H_2}^0$  and  $S_{H_2}^0$  are the standard enthalpy and entropy. The chemical potential of the dissolved H atom is [16]:

$$\mu_S = H_S - TS_S^{id} + RT\ln\left(\frac{c}{b-c}\right) \quad (9)$$

where  $H_S$  is the enthalpy, and  $S_S^{id}$  is the non-configurational part of the entropy of hydrogen in the solid alloy. The last element in the equation is the configurational part of entropy, where b is the number

of interstitial spaces per metal atom and c is the number of spaces occupied by hydrogen atoms. The equilibrium condition equation can be expressed as follows [16]:

$$\Delta H_S - T\Delta S_S = RT\ln p^{1/2} + RT\ln\left(\frac{b-c}{c}\right) \quad (10)$$

where:

$$\Delta H_S = H_S - \frac{1}{2}H_{H_2}^0 \quad (11)$$

$$\Delta S_S = S_S^{id} - \frac{1}{2}S_{H_2}^0 \quad (12)$$

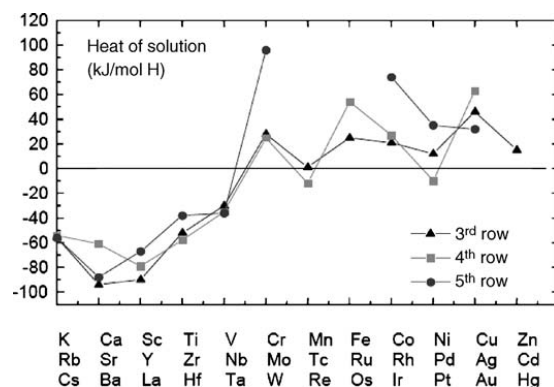
In the case of less dense solutions ( $c < b$ ), the equilibrium condition is described by Seivert's Law, which is Henry's simple law for the dissociation of solutions [17]:

$$p_{H_2}^{1/2} = K_S \quad (13)$$

where  $K_S$  is a constant equal to:

$$K_S = \exp\left\{\frac{1}{RT}(\Delta H_S - T\Delta S_S - RT\ln b)\right\} \quad (14)$$

Seivert's law is valid because hydrogen in gaseous form has the properties of an ideal gas and its molecules are dissociated into atoms before being dissolved in metals [16].



**Fig. 5.** The value of the heat of solution for the elements on rows 3, 4 and 5 of the periodic table, according to Ref. [16]

Figure 5 shows the values of the heat of dissolution for alkali, alkaline earth and transition metals. It is observed that the values for heat are the same for the first three rows of elements in the periodic table. This fact demonstrates how the heat of solutions is determined by the coarse electronic structure of the host metal [16]. From the point of view of the entropy, the biggest contribution is the

configurational entropy loss of gaseous hydrogen and it is approximately constant for all metals ( $\Delta S_s \approx -65 \text{ kJ (molH)}^{-1}$ ) [16].

### 5.1.2. Thermodynamics at high concentration

Usually, the heat of the solution is a function of the hydrogen concentration. For high concentrations, the equilibrium pressure  $P_{eq}$  for phase transformation  $\alpha \rightarrow \beta$  is given by Van't Hoff's law:

$$\ln P_{eq} = \frac{\Delta H}{RT} - \frac{\Delta S}{R} \quad (15)$$

where  $\Delta H$  and  $\Delta S$  are the enthalpy and entropy of the  $\alpha \rightarrow \beta$  transition [16].

In most cases, the change in entropy is given by the loss of standard entropy of hydrogen gas upon contact with the metal structure. Considering this aspect, it can be concluded that the entropy term is not considerably dependent on the nature of the metal and that the  $\Delta S$  term is considered constant. For enthalpy calculations, H-H interactions must be taken into account. We consider that the formation enthalpy ( $\Delta H$ ) of the  $\beta$  phase varies linearly with the hydrogen concentration. The dependence of the enthalpy on  $x$  can be written in the form [18]:

$$\frac{\partial \Delta H}{\partial x} = \left( \frac{\partial \Delta H}{\partial V} \right) \times \frac{\partial V}{\partial x} + \left( \frac{\partial \Delta H}{\partial x} \right) v \quad (16)$$

where:

$$\left( \frac{\partial \Delta H}{\partial V} \right) \times \frac{\partial V}{\partial x} \approx -\gamma K_0 \frac{v_H^2}{v_0} = -u_{els} \quad (17)$$

and  $v_0$  is the atomic volume,  $v_H^2$  it is the increasing volume per hydrogen atom (usually between 2 and 3 Å [19]),  $K_0$  is the bulk modulus and  $\gamma$  is expressed by the relation [16]:

$$\gamma = \frac{2(1-2\sigma)}{3(1-\sigma)} \quad (18)$$

where  $\sigma$  is Poisson's ratio. In general,  $K_0$  is approximately constant with hydrogen concentration. Therefore, for a certain metal, the elastic contribution can be considered constant [16].

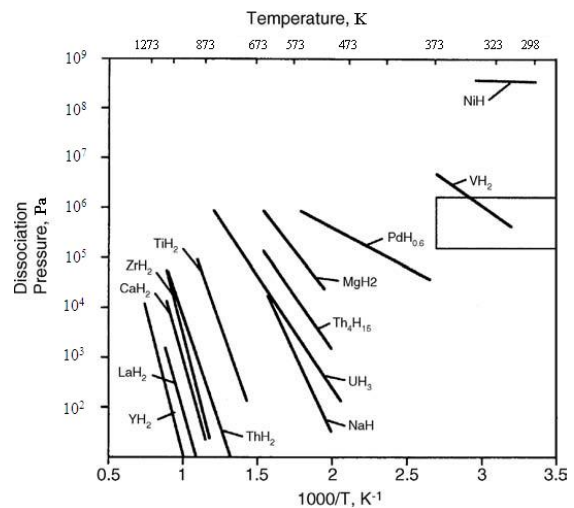
## 6. Intermetallic hydrides

Most of the elements in the periodic table can form hydrides. As can be seen in Figure 6, their dissociation pressures and temperatures are not practical in most applications (temperature between 273-373 K and hydrogen pressure between  $10^5$ - $10^6$

Pa). Vanadium is the only element that meets these conditions, but the hydrogen release capacity is still too low. All these aspects have led to the development of various alloys that meet these conditions and can be applied in practical activities. Compared to the metal-hydrogen system, the alloy-hydrogen system is more complex, because the interstitial spaces have a different chemical and geometric configuration [16].

The first system intended for the formation of intermetallic hydrides was the ZrNi alloy [20]. Later, other magnesium-based alloys were developed that showed an increased potential in hydrogen storage (such as the  $Mg_2Ni$  alloy) [21]. After that, the development and elaboration of hydrides that can be activated at room temperature, such as the ternary systems  $TiFeH_2$  or  $LaNi_5H_6$  began. After the appearance of these ternary systems, a large number of intermetallic hydrides were studied. Compared to metallic hydrides, intermetallic hydrides show increased hydride stability [16].

Generally, intermetallic compounds are formed by combining a metal that easily forms stable hydrides (A) with an element that forms unstable hydrides. Taking into account these aspects, intermetallic compounds can be grouped according to their stoichiometry [16]: 1.  $AB_5$  ( $LaNi_5$ ,  $CaNi_5$ ); 2.  $AB_2$  ( $ZrMn_2$ ,  $ZrV_2$ ); 3.  $AB$  ( $TiFe$ ); 4.  $A_2B$  ( $Mg_2Ni$ ).



**Fig. 6.** Diagram for the dissociation pressure, as a function of temperature and pressure, for some fundamental hydrides, adapted from Ref. [16]

### 6.1. Crystal structure

Ternary hydrides have a different crystal structure with varying symmetries. In most cases, as the hydridation of two-element alloys takes place, the structure expands and deforms, but the crystal structure remains unchanged. However, for some

hydrides of TiFe, Mg<sub>2</sub>Ni, CaNi<sub>5</sub> and LaNi<sub>5</sub> alloys, the crystal structure changes according to the hydrogen content. During the hydrogenation treatment, hydrogen atoms occupy specific interstitial spaces. From the point of view of geometric and calculation aspects for different hydrogen concentrations in hydrides using AB<sub>2</sub> type alloys, the rule was developed that the hole size is a minimum of 0.4 Å, while the minimum bond distance between hydrogen atoms is 2.1 Å. There are some systems that are an exception to this rule and have shown differences due to the difficult structure, determined using neutron diffraction [16].

## 6.2. Electronic structure

The hydride treatment changes the electronic structure of the alloys, these changes can be divided into four categories [22]:

1. the change of electron symmetry and the reduction of the bandwidth caused by the expansion of the crystal structure;
2. the appearance of a hydrogen-metal bond band below the d-band of the metal. Electrons are transferred from the sd band to the new band and some metal states can be pulled below the Fermi level;
3. in hydrides with more hydrogen atoms per measure unit, the HH interaction produces new attributes in the lower portion of the density of states;
4. the general rise above the Fermi level is caused by the inequality between the additional electrons brought by hydrogen and the number of new electron states.

## 6.3. Practical aspects for the use of intermetallic hydrides

In order for intermetallic hydrides to be used on a large scale, transportation, energy systems, etc., certain aspects must be taken into account [16]:

1. alloy/hydride fabrication, if an alloy is synthesized, the next important aspect is activation;
2. activation must be carried out under conditions as similar as possible to thermodynamic equilibrium;
3. hydride/dihydride treatments must be carried out at low pressures and temperatures (from this point of view, metal hydrides are more advantageous than conventional H<sub>2</sub> storage methods);
4. the amount of hydrogen that can be stored by the metal alloy;
5. alloy strength.

## 6.3.1. The development of alloys

As more and more complex hydrides are developed (nanocrystalline, multi-element systems, composites and nanocomposites, graphite/metals or similar hybrid systems, clusters, etc.), it is necessary to take into account the fact that for practical applications, a considerable amount of such materials is needed. However, laboratory technology allows testing and development in this field, which allows obtaining new compounds. When a favourable material for hydrogen storage is found, it will face industrial-scale fabrication [16].

## 6.3.2. Activation of the materials

In order to achieve the activation of metals, we must not neglect the fact that metals can present an oxide layer on the surface, of different thicknesses, which varies depending on the oxidation process of each metal element. This oxide layer acts as a barrier that blocks the interaction of hydrogen with the metal, so it must be removed before hydridation to allow hydrogen gas to come into contact with the material. Considering these aspects, metal activation is recommended to be performed at elevated hydrogen temperatures and pressures, to force hydrogen particles to penetrate the oxide layer and contact the metal. Simultaneously with hydridation, the volume of the material structure increases, and during the dehydration treatment, it returns to its original dimensions. This expansion-contraction process breaks the metal particles, exposes a new metal surface and reduces the particle size [16].

As an example, for the metal alloy Mg<sub>2</sub>Ni, it has been demonstrated in the literature that the activation process is more reliable if mechanical grinding processes were previously performed on the surface of the material [23].

In practical applications, if the material intended for hydrogenation is embedded in a hydrogen storage device, it must be taken into account that the materials from which the respective system is made have considerable resistance at high temperatures and high pressures [16].

## 6.3.3. Hydrogen release capacity

In the case of practical applications, the dehydration process is very important. It is characterized by the reversibility capacity  $\Delta(H/Metal)$  being defined as the bearing width. The reversibility capacity can be considered lower than the maximum capacity  $(H/Metal)_{max}$  [24]. A classic example is vanadium hydride. At 353 K, vanadium forms monohydride VH<sub>x</sub> ( $x \approx 1$ ) at hydrogen pressure



between  $10^{-6}$  –  $10^{-7}$  MPa. At higher pressures (around 1 MPa), vanadium dihydride ( $VH_x$ ,  $x \approx 2$ ) is obtained [16]. In practical applications, the dehydrogenation of vanadium monohydride cannot be realized and it can be concluded that hydrides of the type  $VH_x$  ( $1 < x < 2$ ) show reversibility. The hydrogen storage capacity can be expressed either in the form of atomic ratio (H/Metal) or by mass percentages (wt.%) [16]. The atomic ratio is the number of hydrogen atoms stored per metal atom. The mass percentage represents the amount of hydrogen stored in the hydrate material [16].

### 6.3.4. Hydrogenation kinetics

Hydrogenation is a complex process in which the gas molecules are divided into atoms that form bonds with the crystalline structure of the metal hydride. The overall kinetics is limited by the slowest step, called the rate-limiting step. For the research and development of new alloys, it is recommended that the transported mass and heat do not constitute the speed-limiting step [25]. Taking into account these aspects, it should be considered that the design of the sample ensures a maximum value of thermal conductivity and a minimum value for the resistance to the flow of hydrogen [16].

For the characterization of metal hydrides, the kinetic curve for a given reaction is the transformed fraction as a function of time. The dependence of the curve on pressure and temperature must be studied to deduce the rate-limiting steps of the reaction. For the hydrogen-metal system, the situation is more complicated due to the heat of the reaction, the fast reaction rate, and the low thermal conductivity of the hydride phase. Other factors that can influence the hydridation kinetics curve are sample size, particle size, surface properties and metal and gas purity [16].

## 7. Conclusions

Hydrogen is a clean energy source of high interest in contemporary times. Currently, several  $H_2$  production projects are being debated, with the aim of being used as an energy source in industries such as transport, heat generation and electricity production. Starting from 2022,  $H_2$ -powered vehicles are used and sold in Australia. They have an autonomy of 900 km and a refuelling time of only 5 minutes.

At the global level, research and development works are continuously carried out for hydrogen storage and transportation systems, reliable from several points of view (safety, economics, etc.). Metal hydrides are more advantageous than conventional hydrogen storage in pressure vessels, because of the higher gas storage capacity per unit volume.

Also, in the process of developing an alloy intended for hydrogen storage, aspects such as the hydrogen storage capacity, the conditions under which the hydride reaction is carried out (temperature,  $H_2$  pressure), the ability of the formed hydride to release hydrogen must be taken into account during dehydrogenation, life resistance to hydrogenation-dehydrogenation cycles, the possibility of being produced in industrial quantities, an easy production process, etc.

Taking into account the fact that hydrogen is considered to be a favourable energy source for the future, further global research, development, testing and implementation of hydrogen storage and transportation systems are needed.

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