HYDROGEN IN ZIRCONIUM
Part 1

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The data on hydrogen behavior in zirconium have been systematized. The proposed study deals with a number of basic physicochemical characteristics of the two participants in the Zr–H (H and Zr) reaction, as well as the basic data on Zr–H system in whole. The data on hydrogen atoms position in Zr lattice (predominantly tetragonal voids) and its dynamics are provided. It should be noted that whether the zirconium-dissolved hydrogen has a state of neutral atoms H₀ or ions (H⁺, H⁻, Hδ⁻, Hδ⁺) is a disputable question, while it is clearly stated that hydrogen is not found in zirconium in the molecular state and does not form bubbles filled with molecular hydrogen gas. The basic principles of interaction of hydrogen with metal (M) are reported. The study presents thermodynamics of hydrogen adsorption and absorption by zirconium. Great attention is paid to the correlation characteristics of M–H system interaction with M position in the periodic table, and evaluating implementation of these correlations with respect to the Zr–H system. The data on the diffusion mobility of hydrogen in zirconium are provided. The collected data are aimed at creating a source data base on interaction in Zr–H system required for investigations on delayed hydride cracking.

INTRODUCTION

More than a semicentennial experience of water-cooled reactors operation demonstrated, sometimes painfully, that hydrogen, accumulated in zirconium structural components (ZSC) in operation, upon reaching a critical density (total or local) is one of the main limiting state criteria of these components [1], [2]. The danger is also aggravated by the fact that the presence of hydrogen in zirconium structural components (ZSC) accumulated during operation, may adversely impact the fuel assembly zirconium components during the subsequent operations of spent nuclear fuel (SNF) handling and long-term storage [3].

The main hydrogen-degradation effects in ZSC during operation are: hydrogen embrittlement (sharp ductility decrease during hydriding), formation of large, massive hydrides (corona defects, blisters) (Fig.1) and delayed hydride cracking (gradual stepped crack growth, induced by simultaneous stress and hydrogen effects) (Fig. 2). Each of these phenomena is based on physicochemical interaction of hydrogen with zirconium: physical adsorption, chemisorption, hydrogen dissolution and diffusion, hydride formation, etc. [4]. That is why, development of a delayed hydride cracking (DHC) concept being the matter of our investigation, must be preceded and supported by the data on chemophysical interaction of hydrogen with zirconium. Some of the information search results that are being carried out in this direction are presented here.

In the present investigation, the issues related to hydride crystallography and the properties of zirconium hydrides are discussed only insofar as it is required to develop a basic understanding of the hydrogen/zirconium interaction. We proceeded from the paper size restriction, and the fact that fundamental reviews on the structure and properties of binary hydrides (including zirconium hydrides) were earlier made by Puls [8], Andriyevskiy and Umanskiy [9], [10].
1 HYDROGEN

1.1 Atomic Hydrogen

Hydrogen is the simplest in structure, the smallest and lightest of atoms containing one proton and a single electron. Paradoxically, this simplicity of electronic structure brings about the unique consequences in respect to chemical and physical properties of the element (its atoms, cations and anions) [11]. In its tendency to a completely vacant or completely filled shell, hydrogen, generally, exhibits three oxidation states: +1, 0, -1, corresponding to electron configurations 1s⁰, 1s¹ and 1s², respectively. A number of transformations of atomic hydrogen H⁰ (protium) into hydride-ion H⁻¹ are associated with a fractional change in a number of electrons around the nucleus. During such transformations, the particle size changes considerably. The radius of atomic hydrogen H⁰ is 0.10 nm [12]. Attachment of an electron to a hydrogen atom results in a considerable increase in its size: a hydride-ion H⁻¹ radius in a free state equals 0.208 nm [12], [13]. However the most notable change in size occurs during the ionization of hydrogen atoms (H⁰→H⁺), which leads to a smaller radius of 0.84184·10⁻⁸ nm [14]. Such difference in size between an atom and its cation (5 orders) is unique. Next 1s element - lithium changes its radius only from 0.155 nm for Li⁰ to 0.068 nm for Li⁺.

Atomic radius of hydrogen in the molecular H₂ (covalent bond) equals 0.037 nm [11]. Despite its apparent completeness, atomic hydrogen (H⁰) is an unstable condition. Being in contact with other atoms or molecules, it will certainly react to form a covalent, proton (cation H⁺) or anion (H⁻) bond.

Big values of the first ionization energy I = 1312 kJ/mole (13.60 eV) and electron affinity AE= 72.8 kJ/mole (0.75 eV) evidence of a significant difference between the chemical properties of H⁺¹ and H⁻¹ (Fig. 3) [11]. The binding force of electron with H⁰ decreases considerably in the order: H⁺¹ > H⁰ > H⁻¹. The result demonstrates the exciting dual physical and chemical properties of hydrogen - it is a strong cation for nonmetals, and a weak anion for metals.

\[ E, \text{ eV} \]

\[ +13.60 \]

\[ 0 \]

\[ -0.75 \]

\[ +1 \]

\[ 0 \]

\[ -1 \]

\[ n \]

![Fig. 3. Hydrogen energy H⁰ versus oxidation state n. Dotted lines – a derivative of the electron binding force with H⁰ by electron density. The electron binding force decreases significantly in the order H⁺¹ > H⁰ > H⁻¹ [11]](image)

The H–H bonding enthalpy in H₂ is 436 kJ/moleH₂ or 4.52 eV, which is quite close to a strongly bonded oxygen molecule (498.4 kJ/mole or 5.17 eV).

H⁺¹ and/or H⁻¹ atomic charge changes in accordance with the following reactions [11]:

\[ \text{H}^+ \rightarrow \text{H}^0 + e^-(\Delta H = +0.75 \text{ eV}); \] (1)

\[ \text{H}^+ + e^- \rightarrow \text{H}^0 (\Delta H = -13.60 \text{ eV}); \] (2)

\[ 2\text{H}^0 \rightarrow \text{H}_2 (\Delta H = -4.52 \text{ eV}); \] (3)

\[ \text{H}^+ + \text{H}^0 \rightarrow \text{H}_2 (\Delta H = -17.37 \text{ eV}). \] (4)

A specific position in the periodic table implies a very significant energy difference between the two states: H⁺¹ and H⁻¹ (Eₓ⁺+Eₓ⁻ = 1384.8 kJ/mole (14.35 eV)), resulting in a wide variety of its bonds and phenomena with participation of hydrogen, and certain tendencies in interactions of the element under study with hydrogen, depending on its position in the periodic table [11].

The basic data about atomic hydrogen, which determine the character and intensity of its interaction in contact with other elements, are provided in Table 1.
As already stated, hydrogen atoms cannot bear loneliness; the normal state of hydrogen is H₂(g).

### 1.2 Molecular Hydrogen H₂

Hydrogen molecule H₂ – is a classic example of a covalent bond that is based on the exchange forces [28]. Under normal conditions, molecular hydrogen is a combination of the two isomers: ortho- and parahydrogen [29]. Nuclear magnetic moments (spins) of orthohydrogen (o-H₂) have a similar orientation, while those of parahydrogen (p-H₂) have an opposite orientation. Normal hydrogen gas contains ~ 75 % of o-H₂ and ~ 25 % of p-H₂ [29]. Conversion of o-H₂ into p-H₂ is accompanied with heat production (~ 1400 kJ/mole), which, however, does not occur without catalysts.

The main properties of molecular hydrogen are presented in Table 3.

### Table 3

**Molar Properties of Molecular Hydrogen**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass</td>
<td>2.01594 [30]</td>
</tr>
<tr>
<td>Absolute mass</td>
<td>3.497·10⁻² kg [16]</td>
</tr>
<tr>
<td>Ionization potential</td>
<td>I = 15.426 eV [31]</td>
</tr>
<tr>
<td>Electron affinity</td>
<td>EA = -0.7 eV [29]</td>
</tr>
<tr>
<td>Bond length</td>
<td>0.07416 nm [4]</td>
</tr>
<tr>
<td>Bond energy</td>
<td>-4.748 eV [4],[30]</td>
</tr>
<tr>
<td>Dissociation energy</td>
<td>4.748 eV [4], [30]</td>
</tr>
<tr>
<td>Vibration energy</td>
<td>0.5160 eV [4], [30]</td>
</tr>
<tr>
<td>Rotation energy</td>
<td>0.00732 eV [4], [30]</td>
</tr>
<tr>
<td>Density in gaseous state</td>
<td>0.0899 kg/m³ [12]</td>
</tr>
<tr>
<td>Density of liquid hydrogen</td>
<td>70.811 kg/m³ [12]</td>
</tr>
</tbody>
</table>
High value of the ionization potential I and negative value of electron affinity EA characterize H₂ as a weak electron-donor-acceptor [29], [31], [32]. Electron detachment naturally weakens the H–H bond (Table 5), but electron transfer to the antibinding σ*- MO is much more effective in doing so, decreasing the bond dissociation energy H–H (E₀) (Table 4) [29].

Table 4
Characteristics Of Bonding Forces in Molecule H₂ And Its Ionization States [29]

<table>
<thead>
<tr>
<th>Molecules and Ions</th>
<th>E₀, kJ/mole</th>
<th>l_H-H, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>436</td>
<td>0.074</td>
</tr>
<tr>
<td>H⁺</td>
<td>259</td>
<td>0.107</td>
</tr>
<tr>
<td>H₂⁻</td>
<td>231</td>
<td>0.086</td>
</tr>
</tbody>
</table>

A number of molecular hydrogen properties are worth special consideration [16]:
- very small size (H–H distance is only 0.074 nm);
- strong influence of nuclear magnetic moments (spins) forming the two isomers: ortho- and para-hydrogen, with general symmetric and antisymmetric nuclear spins, respectively;
- low electron density;
- ability to dissociate into atoms.

1.3 Standard Thermodynamic Properties of Hydrogen

For prediction of possibility and completeness of chemical reactions, as well as for state diagram calculations it is necessary to know the initial values of thermodynamic functions and constants for these calculations. The most frequently required data are: standard enthalpy of formation ΔH°(298.15), standard entropies S°(298.15) and standard heat capacities C_p° (298.15).

Table 5 lists the standard thermodynamic properties of hydrogen (properties of H, H⁺, H², H₂ at the temperature of 298.15 K and pressure of 0.1 MPa) [33].

Table 5
Standard Thermodynamic Properties of Hydrogen [33]

<table>
<thead>
<tr>
<th>State</th>
<th>C_p°(298.15), J/mole K</th>
<th>S°(298.15), J/mole K</th>
<th>H°(298.15), kJ/mole</th>
<th>ΔH°(298.15), kJ/mole</th>
<th>ΔG°(298.15), kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>20.786</td>
<td>114.716</td>
<td>6.197</td>
<td>217.999</td>
<td>203.278</td>
</tr>
<tr>
<td>H₂</td>
<td>28.836</td>
<td>130.68</td>
<td>8.467</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>H⁺</td>
<td>20.786</td>
<td>108.946</td>
<td>6.197</td>
<td>1536.246</td>
<td>1516.990</td>
</tr>
<tr>
<td>H₂⁻</td>
<td>20.786</td>
<td>108.960</td>
<td>6.197</td>
<td>139.032</td>
<td>132.282</td>
</tr>
</tbody>
</table>

2 ZIRCONIUM

The basic information about zirconium, which determines its interaction with hydrogen, is provided in Table 6.

Table 6
Some Characteristics of Zirconium

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Weight</td>
<td>A = 91.224 [15]</td>
</tr>
<tr>
<td>Atomic number</td>
<td>Z = 40 [15]</td>
</tr>
<tr>
<td>Group</td>
<td>IV</td>
</tr>
<tr>
<td>Subgroup</td>
<td>IVB – American designation; IVA – European designation</td>
</tr>
<tr>
<td>Electron Configuration</td>
<td>[Kr] 4d² 5s² [15]</td>
</tr>
<tr>
<td>Spin</td>
<td>5/3 [15]</td>
</tr>
<tr>
<td>Magnetic Moment</td>
<td>-1.303 μN [15]</td>
</tr>
<tr>
<td>Electron Affinity</td>
<td>EA=0.427±0.014 eV [18], [34]</td>
</tr>
<tr>
<td>Electronegativeness (Pauling Scale)</td>
<td>1.33 [35]; 1.4 [36]</td>
</tr>
<tr>
<td>Electronegativeness (Alfred Rochow Scale)</td>
<td>1.22 [37]</td>
</tr>
<tr>
<td>Atomic Radius</td>
<td>R=0.160 nm [38]</td>
</tr>
<tr>
<td>Ionic Radius</td>
<td>r(Zr⁺) = 0.114 nm; r(Zr²⁺) = (0.087±0.007) nm; r(Zr³⁺) = (0.079±0.005) nm; r(Zr⁴⁺) = (0.072±0.007) nm [39]</td>
</tr>
<tr>
<td>Molar Volume</td>
<td>14.02·10⁻⁹ m³/mole [38]</td>
</tr>
<tr>
<td>α→β- Transition Temperature</td>
<td>T_αβ= (1135±10) K [33]</td>
</tr>
</tbody>
</table>
Standard thermodynamic properties of zirconium are presented in Table 7.

### Table 7

<table>
<thead>
<tr>
<th>Material</th>
<th>$C_J$(298.15) J/mole K</th>
<th>$S_J$(298.15), J/mole K</th>
<th>$H^\circ$(298.15), kJ/mole</th>
<th>$\Delta H^\circ$(298.15), kJ/mole</th>
<th>$\Delta G^\circ$(298.15), kJ/mole</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr</td>
<td>25.202</td>
<td>38.869</td>
<td>5.497</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

### 3 Zr–H SYSTEM

#### 3.1 Zr–H System Phase Diagram

At present, the majority of metal-hydrogen binary systems phase diagrams are known [44]. The Zr–H system phase states were among the first to be investigated [24]. The Zr–H system phase diagram is constantly updated, a procedure for the line position (interfaces) calculation on the phase diagram has been elaborated well [45].

As of today, four phases are considered to be the equilibrium phases (Fig. 4) [46 - 50]: hydrogen solid solution in close-packed hexagonal α-Zr; hydrogen solid solution based on high-temperature body-centered cubic phase β-Zr; nonstoichiometric dihydride δ-ZrH$_2$, with a face-centered cubic (FCC) Zr sublattice; and dihydride ZrH$_3$, with a tetragonal (FCT, c/a < 1) lattice, with a homogeneity area extending up to the stoichiometric composition (x = H/Zr = 2). The ε-phase forms from the δ-phase at the δ-hydride martensitic transformation [50]. The high-temperature β-Zr phase is in the eutectoid equilibrium with α-Zr(H) and δ-ZrH$_2$, at a point position: T = 547 °C and x = 0.5. Besides, under certain conditions, a metastable γ-phase with a tetragonal (FCT, c/a > 1) lattice is formed which dissociates into α-Zr + δ-ZrH$_2$, with a temperature rise up to 255 °C [46].

![Fig. 4. Zr-H Phase Diagram [46]](image_url)
Crystallographic data on the Zr–H systems phases are given in Table 8. Depending on the influence on the polymorphic transformation in Zr, all of the alloying elements and additives are subdivided into α- and β-stabilizers. Hydrogen refers to very strong β-stabilizers – with an increase in hydrogen concentration, the α→β transition temperature decreases from 863 °C for unalloyed Zr to ~ 547 °C with a hydrogen concentration in Zr of ~ 6 at.% [48 - 49].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Structure</th>
<th>Pearson Symbol</th>
<th>Space Group</th>
<th>Point Group</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Zr</td>
<td>Zr</td>
<td>FCC</td>
<td>hP2</td>
<td>P6/mmc (№194)</td>
<td>D1h; 6/mmm</td>
<td>a = 0.3232 nm; c = 0.5147 nm [41]</td>
</tr>
<tr>
<td>β-Zr</td>
<td>Zr</td>
<td>BCC</td>
<td>ctI2</td>
<td>Im3m (№229)</td>
<td>O_6h; m3m</td>
<td>0.36090 nm at 862 °C, 0.35453 nm at 20 °C [42]</td>
</tr>
<tr>
<td>δ</td>
<td>ZrH_{1.66}</td>
<td>FCC</td>
<td>cF14</td>
<td>Fm3m (№225)</td>
<td></td>
<td>0.4781 nm [41]</td>
</tr>
<tr>
<td>ε</td>
<td>ZrH_{2}</td>
<td>FCT</td>
<td>tI6</td>
<td>I4/mmm (№139)</td>
<td>D_{4h}; 4/mmm</td>
<td>a = 0.3520 nm; c = 0.4450 nm [41]</td>
</tr>
</tbody>
</table>

Metastable Phases
<table>
<thead>
<tr>
<th>Phase</th>
<th>Formula</th>
<th>Structure</th>
<th>Pearson Symbol</th>
<th>Space Group</th>
<th>Point Group</th>
<th>Lattice Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ</td>
<td>ZrH</td>
<td>FCT</td>
<td>tP6</td>
<td></td>
<td></td>
<td>a = 0.3520 nm; c = 0.4450 nm [41]</td>
</tr>
</tbody>
</table>

Zr saturation with hydrogen at a temperature slightly lower than that of the α→β-transition (for example, at 800 °C) results in concentration transformation, being a transition from α to a two-phase (α+β)-field with subsequent transition to a single-phase β-field at further increase in hydrogen content [51].

In α-Zr, thermal solubility of hydrogen is very low, it is ~6 at. % (~600 ppm) at the eutectoid transformation temperature and it decreases rapidly with decreasing temperature (Fig. 5) [45]. At room temperature, solubility of hydrogen α-Zr does not exceed 1 ppm [48].

![Fig. 5. Thermal solubility of hydrogen in α-Zr [45]](Image)

Kearns [52] has systematized and analyzed the data on thermal solubility of hydrogen in Zr, obtained from investigations of hydrogen absorption and diffusion in zirconium under isothermal conditions. He obtained the following equation, describing the temperature dependence of hydrogen on the boundary α/α+δ\(_{H}\alpha=\delta\):

\[ C_{H}^{\alpha/\alpha-\delta} (ppm) = 1.61 \cdot 10^{6} \exp \left(-37447/RT \right), \]

where \( C_{H}^{\alpha/\alpha-\delta} \) is the concentration of hydrogen on the boundary α/α+δ (ppm); A and B are constants; \( R \) is the gas constant (\( R = 8.314462 \) J/(mole·K)).

In a high-temperature β-Zr (BCC), up to ~ 50 at.% of hydrogen dissolves [48].

Systematization and critical analysis of the isothermal absorption curves with empirical fitting of line positions on the phase diagram was done by Zuzek et al. [48], [49].

Great attention is being paid to creation of data bases for thermodynamic description of phases and Zr–H system phase diagram calculation which was well reported for the Zr–H system in [45]. For description of thermodynamic state of solid solutions and zirconium hydrides, the sublattice Hillert and Staffansson model is used [53], where solid solutions of hydrogen in zirconium are considered as compounds with two sublattices, one being filled

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1Hereinafter, except where otherwise specified, ppm-part per million.
completely with metal atoms, and the other one – with interstitial atoms (H) and vacancies, designated V_{iH}. The calculation methods used in [45] and thermodynamic parameters of phases that are formed in the Zr–H system are normally taken as a basis for thermodynamic calculations [54].

As noted above, the basic information for plotting a phase diagram is the data on hydrogen absorption.

3.2 Hydrogen Absorption By Zirconium

Hydrogen absorption (dissolution, occlusion) by metal is hydrogen transition from H\textsubscript{2} into metal. The term “absorbed hydrogen” means all absorbed hydrogen contained both in solid solution, and in hydrides. Solubility is a hydrogen concentration limit in solid solution. Hydrogen capacity is a maximum amount of hydrogen that can be absorbed by the metal under consideration.

The process of hydrogen absorption includes stages as follows:
- molecular hydrogen approaches the surface;
- accumulation of hydrogen molecules on the surface and their dissociation (physical adsorption, dissociation and chemical adsorption (chemisorption) of hydrogen molecules);
- relocation of hydrogen atoms by volume (diffusion);
- formation of hydrides upon reaching the hydrogen solubility limit in the hydride-forming metals, such as zirconium.

3.2.1 Hydrogen Adsorption on Zirconium

The basic reactions on gas/metal surface are shown in Fig 6.

![Fig. 6. Reactions on gas/surface surface](image)

Adsorption reaction:

\[ H_{2} + 2 \text{(two adsorption points)} \rightarrow 2H_{ads} \]  \hspace{1cm} (6)

It should be noted, that there are no special forces which induce adsorption [55]. Hydrogen molecules adsorption on a solid body surface occurs at the expense of hydrogen atoms attraction by adsorbent surface atoms. Gas molecules can be adsorbed on the surface both at the expense of physical and chemical adsorption. Physical adsorption is based on the Van der Waals bond between molecular hydrogen and atoms. In this process, a hydrogen molecule interacts with several adsorbent atoms. The potential energy of a molecule is minimal at the distance of about one radius of an adsorbate molecule (0.2 nm) [12], [56]. The energy of physical adsorption is normally negative; its value in modulus does not exceed 20 kJ/mole H (-0.2 eV). For many metals, the physical adsorption energy is close to -5 kJ/mole H (-0.05 eV) [12]. Since the interaction is weak, a significant physical adsorption takes place only at low temperatures (< 273 K) [56], [57].

Another stage of metal-hydrogen (M–H) reaction: a hydrogen molecule dissociates, and atomic hydrogen overcomes the energy barrier. This process is known as chemisorption. Its energy is normally negative, and the values are from -20 to -400 kJ/mole H. For many metals and for carbon, the chemisorption energy is close to -50 kJ/mole H [12].

Upon dissociation and overcoming the energy barrier, hydrogen atoms diffuse into the bulk.

A diagram representation of the molecular hydrogen potential energy, and the reactions of interaction between molecular and atomic hydrogen with metal atoms is shown in Fig.7 [58].

Zirconium belongs to the metals featuring very active chemical adsorption [59], [60]. Naito [60] determined by kinetic parameters of hydrogen adsorption, that the hydrogen adsorption energy on polycrystalline α-Zr equals -2.84 eV; the bonding force of subsurface layer atoms with their surroundings only slightly differs from the surface atoms bonding force (the bonding energy difference makes only 0.06 eV); the activation energy for adsorption of hydrogen atoms equals -0.02 eV, the energy of atomic diffusion to the bulk equals 0.475 eV. The obtained results demonstrate that hydrogen penetrates zirconium easily, and the process of hydrogen adsorption by zirconium is controlled by the volume diffusion of hydrogen atoms. According to the theoretical estimates reported in [61], the
enthalpy of hydrogen chemisorption on zirconium in both the tetrahedral and octahedral voids for the two surface layers is equal to -3.00 eV.

\[
E_{\text{pot}} = k_{\text{ab}} t.
\]

where \( C_{\text{H}} \) is the quantity of absorbed hydrogen, \( k_{\text{ab}} \) is the parabolic velocity constant:

\[
k_{\text{ab}} = k_0 \exp \left( \frac{-E_{\text{ab}}}{RT} \right).
\]

In accordance with a theoretical evaluation performed by P. Zhang and his colleagues [61], the process of adiabatic dissociation in the \( \text{H}_2/\text{Zr}(0001) \) system has a low barrier (0.05 eV) along the almost stable energy channels; the dissociation of \( \text{H}_2 \) molecules into atoms takes place at a distance of 0.2 nm over the \( \text{Zr} \) (0001) surface.

The initial stages of hydrogen interaction with the \( \text{Zr} \) (0110) surface at 100, 293 and 370 K were investigated by P. Zhang and his colleagues [62] using the NRA (NRA – Nuclear reaction analysis), AES (AES –Auger electron spectroscopy), work function measurements and SSIMS (SSIMS –static secondary ion mass spectroscopy) methods. According to the results obtained, the coefficient of hydrogen attachment to \( \text{Zr}(10\bar{1}0) \) surface at 100, 293 and 370 K is 1; 0.71 and 0.5, respectively. The hydrogen concentration on the surface first rapidly increases, and then passes into saturation. The surface barrier height is 42.3 kJ/mole which corresponds to the energy of hydrogen diffusion to volume.

Zhang and his colleagues studied the segregation of H and D to Zr(0001) surface using the NRA, WF, AES and SIMS methods; determined 194 °C (467 K) to be the maximum segregation temperature [63]. It was established that at the temperatures up to 194 °C, in the samples with a 59 ppm hydrogen content, hydrogen diffuses from volume to surface (hydrogen segregation on \( \text{Zr} \) (0001) surface takes place with formation of small hydride-like precipitates), while at higher temperatures, hydrogen moves from surface to volume.

\( \alpha \)-\( \text{Zr} \) (HCP) has a lower value of hydrogen atomic recombination constant as compared to those of the FCC (Ni) and BCC (Al, Fe) metals [64].

Because of the insignificant values of hydrogen atom enthalpy on surface and in subsurface layer, the process of recombination and subsequent desorption of hydrogen atoms in \( \text{H}_2/\text{Zr} \) system at the temperature of ~ 400 K is practically excluded [62].

### 3.2.2 Kinetics of Hydrogen Absorption By \( \alpha \)-\( \text{Zr} \)

Among the transition metals, the best absorbents are the first members, with their d-zone being less than half filled [65]. As the d-zone of a metal is filled with electrons, its absorption capacity decreases. Palladium is an exception, its atoms contain 10 d-electrons, but it is a good absorbent. In full conformity with this mechanism, zirconium easily absorbs hydrogen (Fig. 8) [66 - 69].

The kinetics of hydrogen absorption by zirconium (variation in the quantity of hydrogen accumulated with time, at prescribed time and pressure) was studied in [70 - 72]. In the majority of works, it is reported that the quantity of hydrogen absorbed by \( \alpha \)-\( \text{Zr} \), varies with time according to the parabolic law:

\[
C_{\text{H}}^{2} = k_{\text{ab}} t.
\]

\[
k_{\text{ab}} = k_0 \exp \left( \frac{-E_{\text{ab}}}{RT} \right).
\]
where \( E_{ab} \) – is the energy of the reaction of hydrogen absorption by \( \alpha \)-zirconium.

![Graph showing \( \ln S \) (S – amount of hydrogen in cm\(^3\) capable of absorbing 100 g of metal at 1 atm) versus temperature [69]](image)

According to [71], in the temperature range of 250...425°C, and at the pressure of 1 atm., the reaction of hydrogen absorption by zirconium follows the parabolic law; parabolic velocity constant \((\text{ml/cm}^2/\text{per second})\) is calculated by the equation:

\[
k_{ab} = 2.3 \cdot 10^5 \exp \left(-\frac{71964.8 \pm 836.8}{RT}\right),
\]

where \( R \) – is the gas constant (\( R = 8.31467 \text{ J/(mole K)} \)), and \( 71.9648 \pm 0.8368 \text{ kJ/mole} \) – the reaction energy of hydrogen absorption by \( \alpha \)-Zr.

Certain changes in the absorption kinetics can be caused by the surface condition and oxidation during hydrogenating [72].

Dependence of the rate of hydrogen absorption by zirconium (at the initial hydriding stage) passes through maximum at 500 °C [73].

With an increase of hydriding time, the amount of absorbed hydrogen passes into saturation.

At a given pressure, the absorption capability of zirconium decreases with increasing temperature (see Fig. 8) [66 - 69], which is characteristic of all exothermic reactions (the enthalpy of hydrogen dissolution by zirconium is negative).

Under atmospheric pressure and at the temperature of 20°C, the ultimate quantity of hydrogen absorbed by zirconium equals to 240 cm\(^3\)/of hydrogen per 1 g of zirconium. At 400, 800 and 1100°C, this value is equal to 235, 160 and 40 cm\(^3\)/g, respectively [67].

The optimal zirconium hydriding temperature is 300...400 °C [66].

Unlike nitrogen and oxygen, almost all of the absorbed hydrogen can be removed from zirconium at its heating in vacuum to 1000...1200 °C [66].

### 3.2.3 Thermodynamics of Absorption

#### 3.2.3.1 General Provisions

Judging by the character of chemical bonding, according to accepted classification, all M-H (metal-hydrogen) compounds are subdivided into three main classes:

- ionic hydrides (salts);
- metal hydrides;
- covalent hydrides (molecular compounds).

In full conformity with Zr position in the periodic table (Fig.9), zirconium hydrides refer to metal hydrides [37].

Investigations on metal structure changes at hydriding indicate [74] that insertion of a hydrogen atom in a metal lattice can:
- be followed by a fundamental metal lattice rearrangement, or in other words, changing the type of packing of metal atoms, e.g., transition from the body-centered cubic (BCC) packing in the individual metal structure to the side-centered cubic packing (FCC) in the hydride metal sublattice;
- not result in essential changes in metal structure. In this case, metal atoms packing in the hydride metal sublattice is no different from the packing in the individual metal structure, or only an insignificant deformation of the unit cell of the lattice occurs.

Hydrogen penetration in zirconium lattice upon reaching thermal solubility results in a metal lattice rearrangement (HCP) and formation of hydrides with a different structure (FCC, FCT) [8].

Depending on the thermal effect symbol, there are distinguished the endothermal (with absorption of heat) and exothermal (with heat release) absorptions. The metals, which absorb hydrogen following the endothermal reaction (aluminium, cuprum, ferrum, etc.) do not form hydrides. The metals, which absorb hydrogen following the exothermal reaction (titanium, zirconium, vanadium, niobium, tantalum), form hydrides upon reaching the solubility limit. The absorption symbol (reaction type) is associated with the position in the periodic table: all metals located to the left of Cr, dissolve hydrogen according to the exothermal reaction, the metals located to the right of Cr, follow the endothermal reaction [75].

Dissolution enthalpy changes in 3d, 4d and 5d transition metals is presented in Fig. 10 [76].

The thermodynamic equilibrium in metal-hydrogen (M–H) system is normally represented by the pressure-composition-temperature (P-C-T) diagram (pressure-composition isotherm). Normal view of the pressure-composition isotherm is shown in Fig 11.
The initial sharp rise of the curve corresponds to hydrogen dissolution in the initial phase (normally designated as α). In this area (up to the solubility limit), hydrogen dissolution takes place without significant changes of α-lattice, and the dependence of hydrogen concentration \( C_H \) on pressure is described by Sievert's law:

\[
C_H = K_H P_{H_2}^{1/2},
\]

where \( K_H \) is the Sievert's constant (constant of hydrogen dissolution in α-phase); \( C_H \) is the hydrogen concentration in solid solution; \( P_{H_2} \) is the hydrogen pressure over metal.

Temperature dependence of equilibrium pressure over metal at the stage of hydrogen dissolution in the initial phase solid solution is described by the equation:

\[
\frac{1}{2} \ln \left( \frac{P_{H_2}}{P_0} \right) = \frac{\Delta H_f}{R} - \frac{\Delta S_f}{R},
\]

where \( P_0 \) is the reference pressure (1 atm).

The enthalpy of hydrogen dissolution in α-Zr\( \Delta H_3 = -58 \) kJ/mole·H (-0.601 eV) [76].

Upon reaching the hydrogen solubility limit in α-phase, hydride formation begins. With appearance of the second phase (hydrides, that are normally designated β in the thermodynamic description of M-H system), the pressure over the material being hydrided which is in equilibrium with the solid solution internal pressure), does not change, and further increase in the amount of absorbed hydrogen is not accompanied by a pressure increase (\( α \rightarrow β \)-transition region). The hydrogen concentration in each phase remains constant, however, the volume fraction of each of the phases changes. The equilibrium pressure of hydride formation (\( α(H_3) \rightarrow α+β \)) is described by the Van't Hoff equation [12], [56 - 57]:

\[
\ln \left( \frac{P_{eq}}{P_0} \right) = \frac{\Delta H_f}{R} - \frac{\Delta S_f}{R},
\]

where \( P_{eq} \) is the hydrogen pressure over metal in the two-phase field α-β (on the plateau, Fig. 11, Fig. 10), \( \Delta H_f \) and \( \Delta S_f \) are the enthalpy and entropy of hydride formation.

If we plot the logarithm of hydride formation versus \( 1/T \), we get a line (Van't Hoff plot) as shown in Fig 12. The activation energy of hydride formation from the oversaturated solid solution α is determined from the slope of this plot.
Since entropy change is essentially determined by the change in hydrogen state from the molecular gaseous state to the dissociated in absorbed state, and that is practically the standard hydrogen entropy ($S_0 = 130 \text{ J/mole } \text{ H}_2\times K$), therefore, $\Delta S = -130 \text{ J/mole } \text{ H}_2\times K$ for all M–H systems [12], [56].

The most stable metallic hydrides, for example, HoH$_2$, have the enthalpy of formation $\Delta H_f = -226 \text{ kJ/mole } \text{ H}_2$. The least stable hydrides are FeH$_{1.5}$, NiH$_{1.5}$, and MoH$_{1.5}$ with the enthalpy of formation $\Delta H_f = +20 \text{ kJ/mole } \text{ H}_2$, $\Delta H_f = +20 \text{ kJ/mole } \text{ H}_2$ and $\Delta H_f = +92 \text{ kJ/mole } \text{ H}_2$, respectively [56].

Upon completion of the $\alpha$-$\beta$ transition, dissolution hydrogen in hydride ($\beta$) takes place.

Sometimes, the pressure-composition isotherm has a number of plateaus, which indicate that during hydrogen absorption, M–H system undergoes several two-phase stages.

### 3.2.3.2 Thermodynamics of Hydrogen Absorption By Zirconium

The P–C–T diagrams for Zr–H system are shown in Fig. 13 [48]. Below the eutectic temperature (550 °C), hydrogen concentration in zirconium increases proportionally to $p^{1/2}$, which corresponds to hydrogen dissolution in solid solution $\alpha$-Zr:

$$c_{H}^{\alpha-Zr} = K_{H}^{\alpha-Zr} \sqrt{P_{H_2}}$$

(13)

Temperature dependence of the Sieverts constant for hydrogen dissolution in $\alpha$-Zr is described by the equation [48]:

$$K_{H}^{\alpha-Zr}(T) \left(\frac{[\text{torr}]}{[\text{M}]^2}\right) = 7.854 \times 10^{-5} \exp\left(\frac{6481}{T}\right).$$

(14)

Further there is a plateau, corresponding to the two-phase field $\alpha + \delta$.

Temperature dependence of the equilibrium pressure at formation of $\delta$-hydrides in $\alpha$-Zr [48]:

$$P_{H_2}^{\alpha+\delta}(\text{torr}) = 6.545 \times 10^{14} \exp\left(-\frac{24321}{T}\right).$$

(15)

After that, the pressure increases again with increase of concentration in the single-phase $\delta$-hydride.

At the temperature ranging between 550 and $\sim 750 \text{ °C}$, the absorption isotherms of Zr–H system have two plateaus. One of them corresponds to the two-phase field $\alpha + \beta$, and the other – to the two-phase field $\beta + \delta$. At $T > 750 \text{ °C}$, the first plateau, corresponding to the two-phase field $\alpha + \beta$, disappears, leaving only the plateau which corresponds to the two-phase field $\beta + \delta$.

At the temperatures of 900 °C and higher, hydrogen continuously dissolves in $\beta$-Zr.

The enthalpy values for different reactions in Zr–H system can be obtained by processing the P-C-T curves in accordance with the rules given in Table 9 and in Fig. 14 [78].

![Fig. 13. Pressure-Composition Isotherm of Zr-H System Zr-H [48]](image1)

![Fig. 14. Pressure-Composition Isotherms of Zr-H System; $T_A$<$T_B$<550 °C<$T_C$<$T_D$[78]](image2)

The enthalpy of forming $\delta$-hydride $\Delta H_f^{\delta} = -141 \text{ kJ/mole } \delta$, the free energy of $\delta$-hydride $\Delta G_f^{\delta}$ formation $= -96.2 \text{ kJ/mole } \delta$, the entropy of $\delta$-hydride $\Delta S_f^{\delta}$ formation $= -1513/\text{K-mole } \delta$ [48].

Yao and Wang, and colleagues [79] investigated hydrogen absorption and desorption at 360 °C for the cycle: H$_2$ absorption during 1 hour at 4 MPa / desorption during 1 hour at 0.01 MPa, and found that under such conditions, the unalloyed $\alpha$-Zr absorbs hydrogen easily and rapidly, while the desorption takes place very slowly: $\alpha$-Zr hydrogen absorption rate at 4 MPa equals 0.044 [H]/[M]×s$^{-1}$, its desorption rate at 0.01 MPa is 0.007 [H]/[M]×s$^{-1}$.

The full energy of hydrogen emission from $\delta$-hydride $= 144.7 \text{ kJ/mole } \text{ H}$ [80].

The data on the enthalpy of binary hydride formation depending on the metal position in the periodic system are provided in Fig. 15 [81].
### Thermodynamic Characteristics of Reactions in Zr-H System
(characteristics determined according to P–C–T) [78]

<table>
<thead>
<tr>
<th>Composition (Fig. 14)</th>
<th>f– function depending on →1/T</th>
<th>Enthalpy $= R \frac{d(f)}{d(1/T)}$</th>
<th>Value of reaction enthalpy, kJ/mole</th>
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<tr>
<td>a</td>
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<td>b</td>
<td>lnC</td>
<td>$\Delta H_{a+\delta-Zr}$</td>
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<tr>
<td>g</td>
<td>lnP</td>
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### Group Period

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**Fig. 15. Enthalpy of Binary Hydrides Formation, kJ/moleH₂ [81]**

### REFERENCES


ВОДОРОД В ЦИРКОНИИ
Часть 1
Т.П. Черняева, А.В. Остапов

Систематизированы сведения о поведении водорода в цирконии. Предлагаемые материалы касаются ряда основных физико-химических характеристик двух участников реакции взаимодействия Zr–H (H и Zr), а также фундаментальных данных о системе Zr–H в целом. Приводятся сведения о положении атомов водорода в решетке Zr (преимущественно тетрагональные пустоты) и его динамике. Следует отметить, что дискусионным является вопрос относительно того, имеет ли растворенный в цирконии водород состояние нейтральных атомов H0 или ионов (H+, H+, и H2+), в то же время однозначно утверждается, что водород в цирконии не встречается в молекулярном состоянии и не образует пор, заполненных молекулярным газообразным водородом. Извлекены основные принципы взаимодействия водорода с металлами (M). Представлена термодинамика адсорбции и абсорбции водорода цирконием. Большое внимание уделено корреляции характеристик взаимодействия в системе M–H с положением M в периодической системе элементов и оценке реализации этих корреляций применительно к системе Zr–H. Приведены сведения о диффузионной подвижности водорода в цирконии. Собираемые сведения ориентированы на создание исходной базы данных о взаимодействии в системе Zr–H, необходимой при проведении исследований по замедленному гидридному растрескиванию.

ВОДЕНЬ У ЦИРКОНИИ
Частина 1
Т.П. Черняева, А.В. Остапов

Систематизовані відомості про поведінку водню в цирконії. Пропоновані матеріали стосуються низки основних фізико-хімічних характеристик двох учасників реакції взаємодії Zr–H (H і Zr), а також фундаментальних даних про систему Zr–H в цілому. Наводяться відомості про становище атомів водню в решті Zr (переважно тетрагональні порожнечі) і цього динамічі. Слід зазначити, що дискусійним є питання щодо того, чи має розчинений у цирконії водень стан нейтральних атомів H0 або іонів (H+, H+ і H2+), в той же час однозначно стверджується, що водень в цирконії не зустрічається в молекулярному стані і не утворює пор, заповнених молекулярним газоподібним воднем. Викладено основні принципи взаємодії водню з металами (M). Представлена термодинаміка адсорбції і абсорбції водню цирконієм. Велику увагу приділено кореляції характеристики взаємодії в системі M–H з положенням M в періодичній системі елементів та оцінці реалізації цих кореляцій стосовно до системи Zr–H. Наведено відомості про дифузійну рухливість водню в цирконії. Зібрані відомості орієнтовані на створення вихідної бази даних про взаємодію в системі Zr–H, необхідної при проведенні досліджень по сповільненому гідридному розтріскуванню.