

HYDROGEN AND ITS ISOTOPES IN AND ON METALS

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Abstract

A summary description is given of phenomena related to the surface adsorption and bulk absorption of hydrogen and of its isotopes by a metallic host. Thermodynamic and surface properties, electronic and crystal structure and diffusion are illustrated for the examples of the hydride formation of Pd and of LaNi₅ as typical examples of hydride forming elemental metals and intermetallic compounds.

Introduction

"Hydrogen (deuterium) in and on metals" as a topic attracts metallurgists, solid state scientists, mechanical and chemical engineers, energy technology specialists and nowadays also those scientists who try to clarify the cold fusion phenomena.

Let us consider a metal-hydrogen system. It consists of a metal, of hydrogen in a gaseous or condensed phase and of an interface inbetween. We then ask how hydrogen reacts at the interface with the metal, whether and how hydrogen diffuses into the metal and forms a solid solution, a metal hydride or other types of "hydrogen-metal-alloys". As a metal hydride we define a single phase compound between a host metal and hydrogen, e.g. PdH_{0.6}, MgH₂, LaNi₅H_{6.5}. Then we would like to know the properties of these hydrogen-metal alloys and whether isotope effects appear. Deuterium, tritium and also the positive muon μ^+ are considered as hydrogen isotopes. Finally we have to

ask whether situations may exist in which two hydrogen (deuterium) atoms come closer than 0.35 \AA to raise the fusion rate.

For further reading we recommend [1-5].

Structural and thermodynamic properties

A simplified and frequently used (one-dimensional) model to describe H_2 gas and a hydrogen dissolving metal is shown in Fig. 1. A hydrogen molecule approaching the metal can be dissociated at the interface, adsorbed at appropriate surface and near surface sites and dissolved at interstitial sites of the host metal. If the local hydrogen concentration exceeds a certain limit, a hydride phase precipitates. Upon electrochemical charging an electron transfer reaction converts adsorbed H_2O into adsorbed H and OH^- .

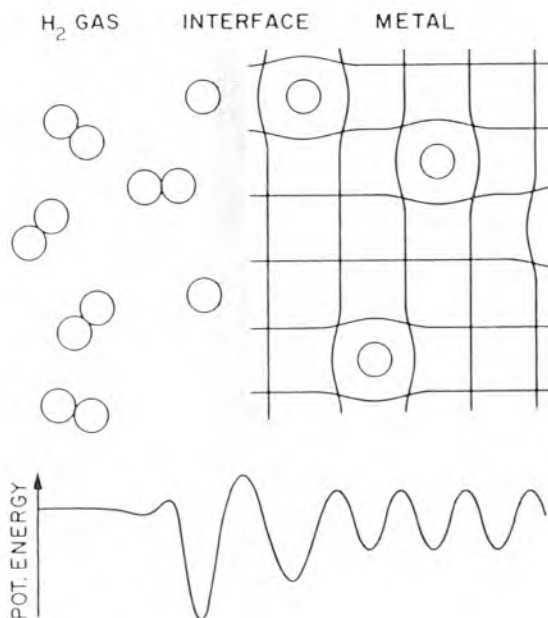


Fig. 1. Simplified model of the dissociation of molecular hydrogen at an interface and of the solution of hydrogen atoms in the bulk, on interstitial sites

The thermodynamic aspects of hydride formation (gaseous hydrogen) can be described by pressure-composition isotherms (pcT curves, Fig. 2). The host metal dissolves some hydrogen as a solid solution (α -phase). As the H_2 pressure, and herewith the concentration C_{H} of dissolved H, is increased, the H-H interaction becomes locally important and nucleation and growth of the hydride phase (β) start.

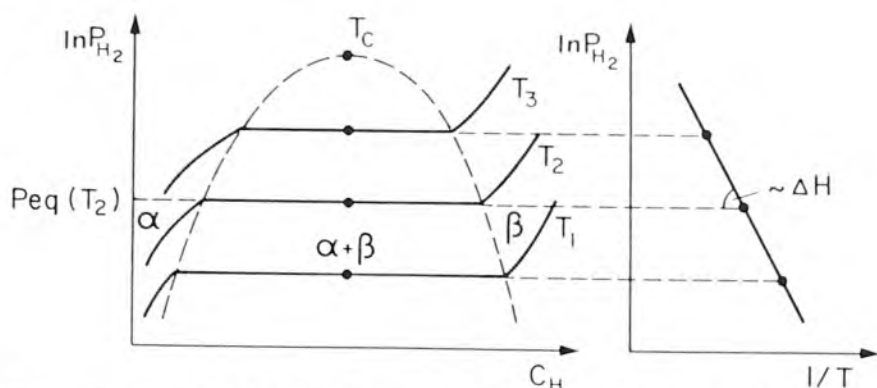


Fig. 2. Pressure-composition isotherms for the solid solution of hydrogen (α -phase) and hydride formation (β -phase). The region of coexistence of the two phases is characterized by the flat plateau at the equilibrium pressure $p_{eq}(T)$ and ends at the critical temperature T_c . The enthalpy of hydride formation ΔH is obtained from the variation of the equilibrium pressure (on a logarithmic scale !) with temperature in a van't Hoff plot [4].

At the electrochemical interface the electrochemical potential replaces $\ln p(H_2)$ in Fig. 2 according to the Nernst equation. While the two phases α and β coexist, the isotherms show a plateau, the length of which determines how much H_2 can be stored reversibly with small pressure variations. In the pure β -phase the H_2 pressure raises steeply with the concentration. At higher H_2 pressure further plateaux and further hydride phases may be formed. The two-phase region ends in a critical point T_c . The plateau pressure $p_{eq}(T)$ strongly depends on temperature. From the slope of a so-called van't Hoff plot of the plateau pressure (on a logarithmic scale) versus T^{-1} , the enthalpy of hydride formation ΔH can be evaluated. At room temperature p_{eq} amounts to and 1.6 bar for Pd and $LaNi_5$, respectively.

Most host metal lattices expand upon the absorption of hydrogen; the crystal structure changes mostly with a reduction of symmetry, a H-sublattice is formed, order-disorder transitions of the H-sublattice occur, lattice defects are formed, strain fields grow, and even non crystalline and probably quasi-crystalline materials can be formed.

The equilibrium pressure $p_{eq}(T)$ for deuterium or tritium absorption is for many metals higher than for hydrogen absorption, the so called normal isotope effect.

The equilibrium position of hydrogen and of its isotopes on interstitial sites is determined experimentally by neutron diffraction. All diffraction pattern measured so far are in agreement with the occupation of interstitial sites by one or zero hydrogen atoms. There is no experimental evidence for "hydrogen clusters" in the same interstitial hole. Upon increasing the pressure additional hydrogen goes into different sites. The

H-H or D-D- separation was never found to be smaller than 2.1 Å in metallic hydrides and 1.87 Å in complex hydrides such as K_2ReH_9 [6].

In the two phase region the expanded hydride phase β and the host metal phase α coexist. In ductile metals like Pd the $\alpha \rightarrow \beta$ transition across the two phase region introduces lattice defects; brittle materials like many intermetallics disintegrate into a powder, a special type of hydrogen embrittlement. $LaNi_5$ disintegrates into powder of $\approx 10\mu m$ grain size and $\approx 0.3 m^2/g$ specific surface area.

Non equilibrium phenomena may be related with that crack formation and propagation upon hydrogen absorption. Among others strong local electric fields were mentioned [7].

Electronic Properties

The dissolution of hydrogen in a metal lattice and the formation of a metal hydride perturbs considerably the electrons and phonons of the host metal. Four different effects are in general relevant for understanding the changes in the electronic structure:

- 1) the generally observed expansion of the lattice often accompanied by a change in the crystal structure results in a modification of the symmetry of the states and in a reduction of the band width.
- 2) The attractive potential of the proton affects those metal wavefunctions which have a finite density at the H site and leads to the so-called metal-hydrogen bonding band below the metal d-band.
- 3) The additional electrons brought by the H atoms into the unit cell result in an upward shift of the Fermi level.
- 4) H-H interaction leads to new features in the lower portion of the electron density of states.

Effect 2), the lowering of host metal states to form the bonding band, corresponds to an exothermic contribution to the enthalpy of hydride formation whereas effect 3), the

upward shift of E_F represents an endothermic contribution. In a first approximation the balance of 2) and 3) decides on the stability of the hydride [8]. The effects are clearly visible in the calculated density of electronic states of Pd and PdH_x (Fig. 3a) and in the measured x-ray photoelectron spectra of the valence band of ZrMn_2 , ZrCr_2 , ZrV_2 and their hydrides (Fig. 3b).

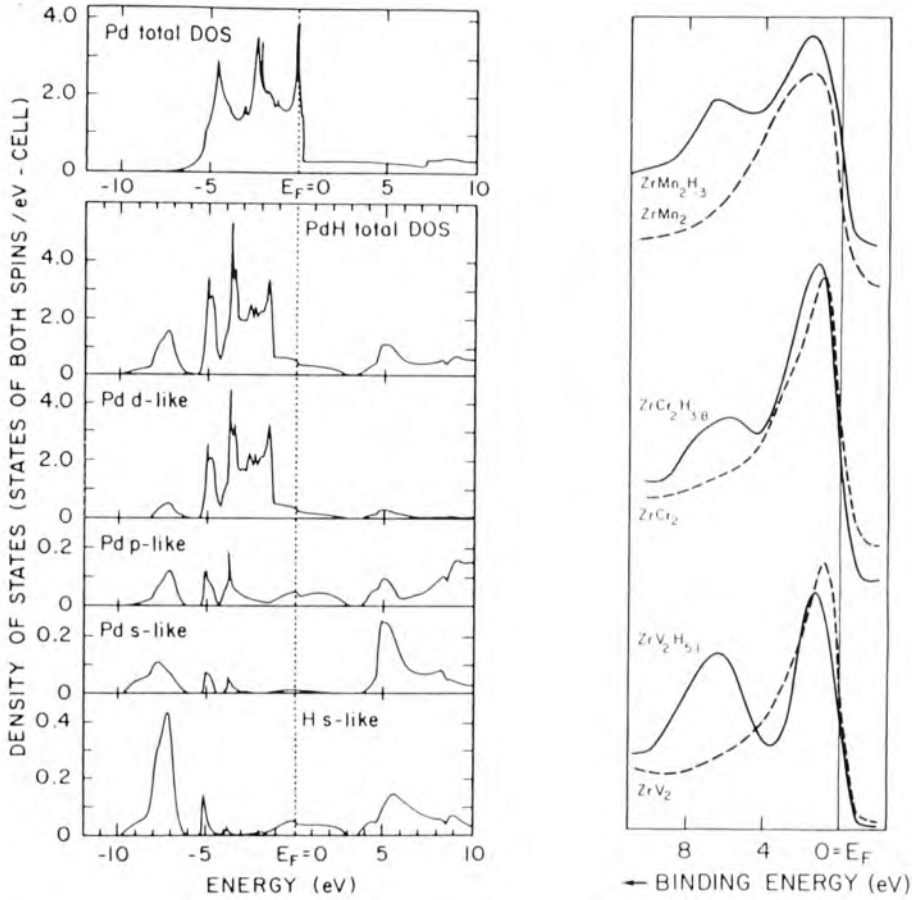


Fig. 3a (left): Calculated total density of electronic states (DOS) of Pd metal (top) and stoichiometric PdH as well as partial DOS of PdH. [8 and ref. cited therein].

Fig. 3b (right): X-ray photoelectron spectra of the valence bands of ZrMn_2 , ZrCr_2 , ZrV_2 and their hydrides [8 and ref. cited therein].

Dynamics and diffusion of hydrogen

Hydrogen atoms dissolved in a metallic host lattice may perform motional processes on very different time scales: They vibrate on interstitial sites at frequencies much higher than the neighbour metal atoms and amplitudes of $\approx 0.1 - 0.2 \text{ \AA}$. After many

oscillations on one site a H atom may jump into another site. Subsequent jumps may lead either to local motions over spatially restricted areas or to long range diffusion.

Diffusion of interstitial H in transition metals and transition metal alloys has been known for a long time to be very fast; the diffusion coefficient D reaches values up to 10^{-4} cm²/s around room temperature (Fig. 4),

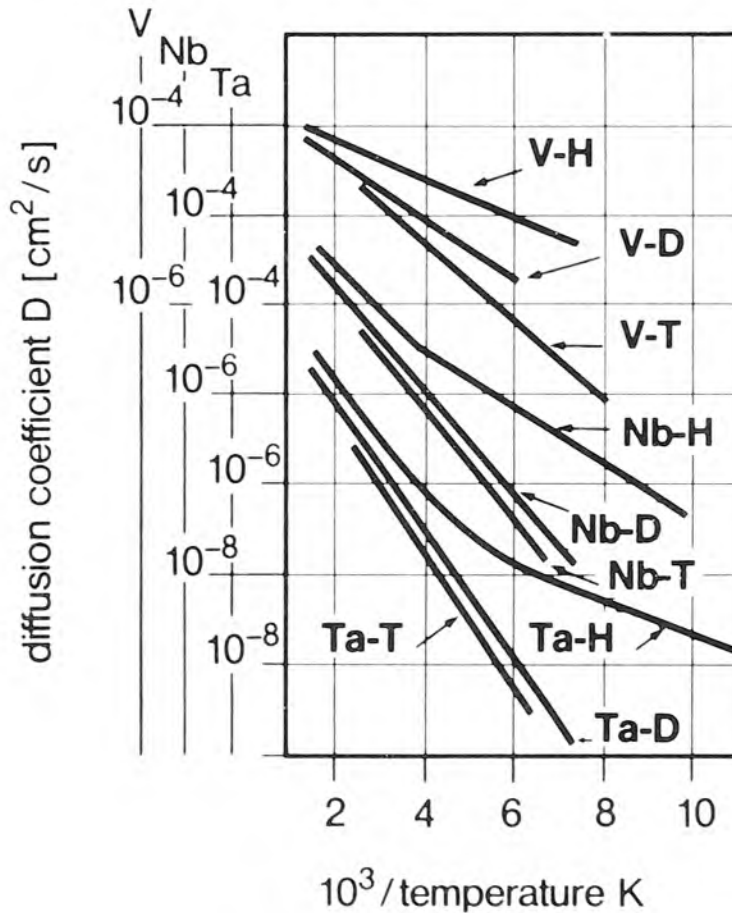


Fig. 4: Diffusion constant of hydrogen, deuterium and tritium in bcc metals as a function of inverse temperature [9].

i.e. values 10 to 15 orders of magnitude higher than for nitrogen or oxygen. In terms of an Arrhenius law $D = D_0 \exp(-E_a/kT)$ the activation energies E_a are very low, of the order of 100-200 meV and account for the high values of the diffusion constants.

The isotope effect observed for D_0 and E_a does not exhibit the behaviour expected for classical jump diffusion. Quantum effects play a significant role. For H diffusion the quantum effects dominate low temperature diffusion; for the diffusion of the light isotope μ^+ they are more pronounced already at higher temperatures.

A discrepancy between measured jump length and distances between interstitial sites lead to the assumption of time correlated jumps according to the following model: the distortion field around an interstitial H atom lowers its potential energy by 0.1 eV relative to that on neighbouring unoccupied sites. If the residence time is much shorter than the lattice relaxation time jumping from an interstitial site into the nearest interstitial site and again into the next nearest interstitial sites may be favorable [9].

The D atom vibrations are not expected to bring D atoms on adjacent interstitial sites significantly closer together.

Surface Properties

The first step in the formation of metal hydrides and solid solutions from molecular hydrogen gas or by electrochemical charging occurs on the surface of the host metals. The interaction with H₂ can consist e.g. of sticking, dissociative chemisorption, surface diffusion and solution in the near surface or bulk region. The H-metal bonding is of electronic nature at the surface as in the bulk.

In order to minimize the free energy of a crystal the equilibrium position of surface atoms is different from that given by the lattice periodicity of the bulk. This surface relaxation often amounts to a 5-10% contraction between the first and second layer without noticeable change in the lateral symmetry. In few cases clean metal surfaces are reconstructed, i.e. the lateral symmetry of the top layers differs from that of the bulk. Upon increasing coverage adsorbed H atoms form disordered or ordered surface phases. The adsorption itself can induce relaxation or reconstruction of the substrate surface or even cancel the relaxation or reconstruction of the clean substrate surface. There is experimental and theoretical evidence that chemisorbed H does not necessarily occupy sites on top of the first metal atom layer, but also sites between and underneath top surface metal atoms. Subsurface H was observed together with a strong surface reconstruction (surface hydride formation). The H-H (and D-D) equilibrium distances are comparable to those between bulk interstitial sites, i.e. $\geq 2 \text{ \AA}$. The distance between planes of surface D and subsurface D e.g. on Pd (111) can be shorter, however, it is unlikely that a surface D sits on top of a subsurface D in thermal equilibrium distribution [10].

Whenever dynamical processes dominate the interaction, isotope effects can occur. They have been reported for the H binding energy, the dynamics of trapping and sticking as well as for surface diffusion. None of them point to extraordinarily short D-D- distances so as to be required to raise the D-D fusion rate.

In studies of the interaction of Pd(100), Pd(110), and Pd (111) with H and D at low temperature (≈ 115 K) an up to 10 times slower rate of filling of α states (bulk H sites) was observed when using D instead of H [11]. These results were obtained on the reconstructed surfaces, i.e. after saturation coverage of the chemisorption sites. That isotope effect is normal in the sense that the higher equilibrium pressure of the D₂-Pd bulk-isotherms cause a higher driving force for D₂ at equal H₂ and D₂ pressure. The size of the effect, however, is larger than expected and might point to strong quantum phenomena.

The influence of a high electric field on the photon stimulated desorption of hydrogen and deuterium from Rh and Ni surfaces yield H⁺, D⁺, H₂⁺ and D₂⁺ as desorbing species and apparently no isotope exchange [12].

Electrode surface contamination by heavy metals

We analyzed the surface of several Pd electrodes after electrochemical charging in D₂O (LiOD) and H₂O (LiOH) at different current densities during some hours up to several weeks. X-ray photoelectron spectroscopy (XPS), which probes the top 20 to 30 Å, was used. Surprisingly, strong Pb contamination of more than one atomic monolayer together with weak Hg and Bi contamination was observed (Fig. 5).

On the Pd electrode of the cold fusion experiment done at PSI (Villigen, Switzerland) we found Zn as major contamination in amounts of several monolayers and some Pb and Hg.

Additional test experiments proofed that the heavy metal impurities originated from D₂O. They were electrochemically deposited on the Pd electrode. It is evident that monolayers of heavy metal impurities change the surface/interface properties of electrodes considerably. Experienced electrochemists may be aware of that problem and clean their electrolytes prior to the experiments.

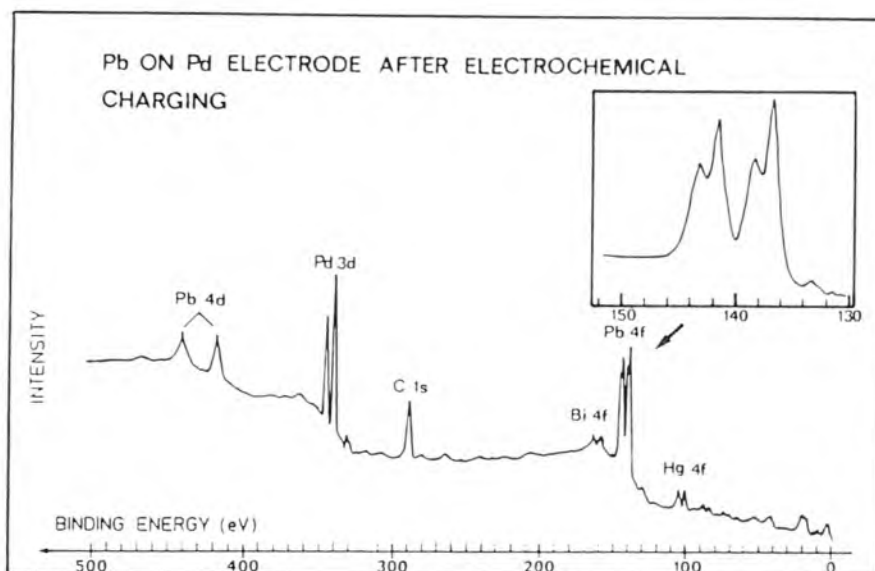


Fig.5. Photoelectron spectrum of a palladium electrode taken after an electrochemical cold fusion experiment in D_2O (LiOD) showing unexpected lead contamination of the order of an atomic monolayer and minor mercury and bismuth contamination as well as the usual carbon contamination. The splitting of the Pb 4f_{7/2} emission into peaks at 136.8 eV and 138.4 eV indicates a mixture of metallic Pb and Pb oxide, resp. [13].

That detection led us to the development of a new extremely sensitive method to detect heavy metal impurities in liquids by electrodeposition and subsequent analysis by XPS [13,14]. The sensitivity is better than 1 ppt.

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