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# Modeling and experimental verification of the thermodynamic properties of hydrogen storage materials

A.V. Ledovskikh<sup>a</sup>, D.L. Danilov<sup>a,b</sup>, M. Vliex<sup>a</sup>, P.H.L. Notten<sup>a,b,\*</sup>

<sup>a</sup> Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

<sup>b</sup> Forschungszentrum Jülich, Fundamental Electrochemistry (IEK-9), D-52425 Jülich, Germany

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## ABSTRACT

A new mathematical model has been developed describing the thermodynamics of the hydrogen absorption and desorption process in Metal Hydrides via the gas phase. This model is based on first principles chemical and statistical thermodynamics and takes into account structural changes occurring inside hydrogen storage materials. A general state equation has been derived considering the chemical potentials of reacting species and volume expansion, from which the equilibrium hydrogen pressure dependence on the absorbed hydrogen content can be calculated. The model is able to predict the classical Van 't Hoff equation from first-principle analytical expressions and gives more insight into the various hydrogen storage characteristics. Pressure-Composition Isotherms have been simulated for various hydride-forming materials. Excellent agreement between simulation results and experimental data has been found in all cases.

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## Introduction

Metal Hydrides (MH) can be successfully employed as efficient and safe storage media of hydrogen gas. In these materials storage takes place under moderate pressure and temperature conditions. In that respect MH have a significant advantage over traditional hydrogen storage systems, which suffer from either extremely high pressures or very low temperatures. Storage in MH is therefore one of the key factors, facilitating e.g. hydrogen-driven fuel cells and Nickel-Metal Hydride (NiMH) batteries [1–7]. In order to unravel the complex hydrogen storage process, a more detailed understanding is, however, essential.

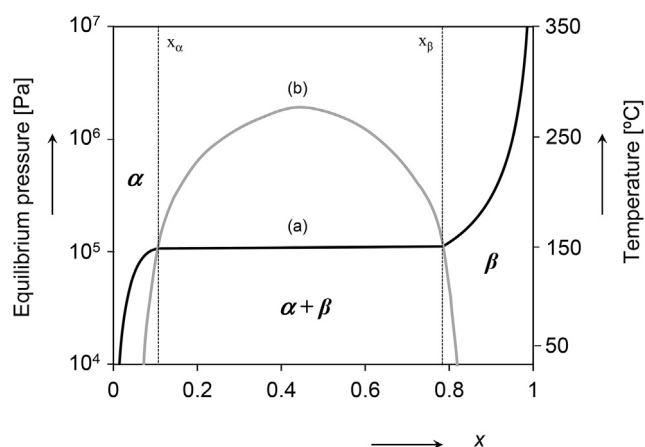
MH materials are generally characterized by pressure-composition isotherms [4–8]. A typical isotherm and corresponding phase diagram for conventional MH alloys are schematically shown in curves (a) and (b) of Fig. 1, respectively [6–9]. The isotherms are generally plotted versus the normalized hydrogen content ( $x$ ). During hydrogen absorption at low concentrations a solid solution is formed, which is generally denoted by the  $\alpha$ -phase. In this concentration region the partial hydrogen pressure ( $P_{H_2}^{eq}$ ) is clearly dependent on the amount of stored hydrogen. After the hydrogen concentration reaches a certain critical value ( $x_c$ ), phase transition is initiated and the  $\alpha$ -phase transforms into the  $\beta$ -phase as indicated in Fig. 2a. The pressure dependence in this two-phase coexistence region is characterized by a (sloping) plateau [10,11].

\* Corresponding author. Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands.

E-mail address: [P.H.L.Notten@tue.nl](mailto:P.H.L.Notten@tue.nl) (P.H.L. Notten).

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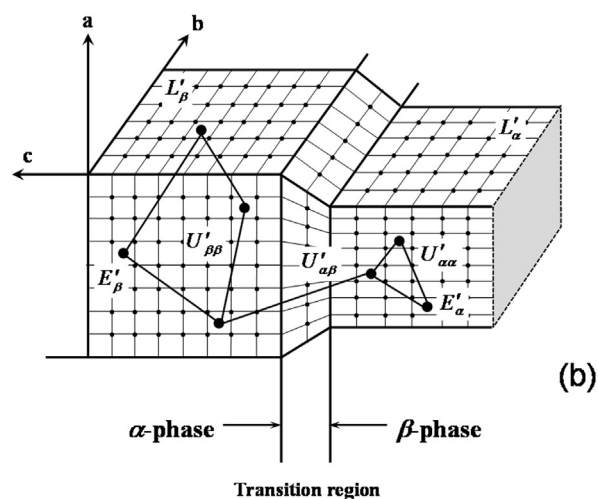
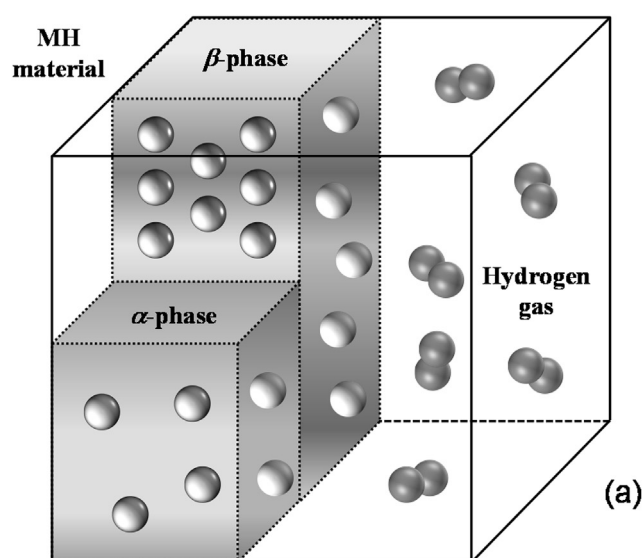


**Fig. 1** – Schematic representation of a pressure-composition isotherm (a) and phase-diagram (b) for a typical hydrogen storage material.  $\alpha$  and  $\beta$  solid solution regions are indicated together with the temperature-dependent two-phase ( $\alpha + \beta$ ) miscibility gap.

Hydrogen absorption induces significant volumetric expansion of the crystal lattice, especially in two-phase coexistence region, as is schematically represented in Fig. 2b [1–4,12]. After the  $\alpha$ -phase has been fully converted into the  $\beta$ -phase at  $x_{\beta}$ , a clear pressure dependence on  $x$  is again found in the solid solution region of the  $\beta$ -phase. The two-phase miscibility gap between  $x_{\alpha}$  and  $x_{\beta}$  decreases at higher temperatures, to completely disappear at the critical temperature (Fig. 1, curve b). Above the critical temperature there is no two-phase coexistence region [6–9,13,14]. Similarly the critical composition and critical film thickness has been identified at which two-phase coexistence region is absent [12,15].

Several attempts have been made to describe pressure-composition isotherms. Existing mathematical models are often based on statistical thermodynamics, allowing simulating macroscopic characteristics by using microscopic parameters, such as atomic interaction energies, etc. One of the first thermodynamic models has been proposed by Lacher [16]. This semi-empirical model successfully described isotherms above the critical temperature but did not give a proper description in the two-phase plateau region. Further improvements of the Lacher-model have been proposed by others [17,18]. These models are, however, based on heuristic assumptions and empirical parameters, and have a high level of mathematical complexity. A different approach has been adopted by Flanagan et al. [3,10,11] who described the thermodynamics of the hydrogen storage system in terms of chemical potential of reactants and reaction products. Similar model with simple atomic interaction energy term has been proposed by McKinnon [19]. Unfortunately these models can only describe isotherms with flat plateau regions, using the so-called Maxwell construction. Attempts to describe sloping plateaus were, however, rather empirical [20].

Recently a Lattice Gas Model (LGM) has been proposed for MH systems [7]. The advantage of this LGM is that phase transitions are included together with (inter-phase)



**Fig. 2** – (a) Schematic representation of the hydrogen storage process. (b) Schematic representation of the lattice gas model in the two-phase ( $\alpha + \beta$ ) coexistence region for a typical hydrogen storage material. The various host energies ( $L'_i$ ), hydrogen guest energies ( $E'_i$ ) and interaction energies ( $U'_{ij}$ ) between hydrogen stored in the different phases are indicated.

interaction energies of hydrogen inside the host material (see Fig. 2b). The excellent agreement between simulation results and experimental data has been shown for various types of MH materials revealing both flat and sloping plateaus [7,15,21]. The original LGM has, however, been developed with the assumption that the change of the Gibbs free energy during the (de)hydrogenation process depends on the materials solid-state properties only and other contributions were therefore neglected. Consequently, the LGM was not able to describe the characteristics of complete hydrogen storage systems, hence excluding the possibility to simulate, for example, the Van 't Hoff equation [5,22].

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