

Metal Hydride Technologies for Separation of Hydrogen Isotopes

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Abstract. The paper considers the issue of theoretical prediction of characteristics at which separation of hydrogen isotopes occurs in the “gas-metal” system.

Mathematical modeling of sorption is based on the use of the lattice gas model often used for metal hydrides. In contrast to the Leicher ideal solution model, it is taken into account that the dissolution of hydrogen in the metal increases the volume of the crystal lattice. This leads to additional contributions to potential energy. The model also takes into account the interaction between the atoms of the incorporated (absorbed) hydrogen isotopes. These phenomena are described by the methods of thermodynamic perturbation theory.

The different composition of the gas (protium and deuterium) in contact with the metal leads to the fact that sorption, accompanied by the formation of hydride, proceeds for the same temperature at different equilibrium pressures. This phenomenon characterizes the isotope effect. The temperature dependences of the pressure on the “plateau” for palladium hydride and deuteride are obtained. The differences in these pressures can be used for the practical use of metal hydrides in the separation of hydrogen isotopes.

Introduction

The ability of transition metals to adsorb hydrogen in significant amounts facilitated their practical application. Moreover, this process is reversible, i.e. the decomposition of the formed metal hydrides is accompanied by the release of accumulated hydrogen.

The use of metal hydrides (MH) as reversible hydrogen sorbents opens up prospects for the creation of new multifunctional heat-using devices for energy and technological purposes [1, 2, 3]. Such devices allow performing the operations of receiving hydrogen, its long-term safe storage, purification (including isotope separation), delivery to the consumer with programmable pressure and flow rate, etc.

The processes of storage and purification of hydrogen are based on the phenomenon of sorption. In particular, the process of separation of hydrogen isotopes in the gas - solid system, which occurs when using MH, is based on the phenomenon of adsorption (absorption of a substance from a solution or gas by the surface of a solid). In this case, the formation of the hydride phase of the metal is accompanied by the dissociation of hydrogen molecules on the surface and the incorporation of atoms into the interstices of the crystal lattice.

The study of the equilibria of the phases formed in such systems is not only of theoretical, experimental, but also practical interest in the light of the use of hydrogen. However, such experimental studies are expensive and time-consuming. Therefore, the method of mathematical modeling of phase equilibria in hydrogen - metal hydrides systems has been used recently. This method allows us to restrict experimental studies and it is used in the present work.

Modeling (lattice gas model, dilatation, intermolecular interaction)

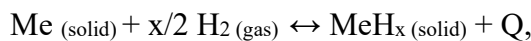
Mathematical modeling of the processes occurring during the absorption of hydrogen by metals makes it possible to replace the study of a complex physical process by the study of a similar process on a simplified model. This will allow predicting the data required for the design of metal

hydride systems. In this case, a comparison of the existing experimental data with the calculated characteristics of metal hydrides should be performed.

Modeling of phase transitions between disordered phases of metal hydrides with different isotopic compositions was performed using a unified method of thermodynamic perturbation theory for both the molecular phase H_2 (D_2) and the hydrogen subsystem of hydrides. In the latter case, within the framework of the model of a nonideal lattice gas of atomic hydrogen, the perturbation theory method makes it possible to adequately take into account the influence of the hydrogen – hydrogen interaction of attraction.

Metal hydride technologies are based on the process of reversible absorption of hydrogen by hydride-forming metals with the formation of metal hydrides.

Let us consider the *modeling* of this process using the example of palladium, which belongs to the group of transition metals. For such metals, hydrides are formed by absorption of hydrogen from the gas phase with the formation of binary hydrides MeH_x



the reaction is reversible, so that small changes in pressure and temperature can reverse the direction of the process.

In general, the reaction proceeds in three stages. At the first stage, adsorbed hydrogen in the metal matrix forms a disordered interstitial solid solution (α -phase). The concentration of dissolved atoms depends on the pressure of hydrogen gas P and its temperature T .

At the second stage of the sorption process, regions of a disordered solid solution also appear, but with a higher concentration (β -phase).

The process proceeds in equilibrium at a constant hydrogen pressure P , which corresponds to the appearance of a plateau on the “pressure – composition” isotherm, i.e., the dependence of the equilibrium hydrogen pressure (P) on its concentration (C) at a constant temperature (T).

The third stage is characterized by the fact that the entire solid solution is converted into hydride. Further sorption of hydrogen is its dissolution in the β -phase of the hydride. In this case, the equilibrium hydrogen concentration increases with increasing pressure, approaching its limit value C_{max} .

The maximum concentration is determined by the sorption capacity of the metal c_s . This parameter is the number of interstices available for hydrogen insertion in the structure of the metal matrix, referred to the number of metal atoms. For the Pd-H system, $c_s \cong 0,6$ [4].

To describe these transformations, a *lattice gas* (LG) or lattice fluid model is used. A lattice gas is a collection of atoms that form their own spatial lattice in the matrix. Phase transitions associated with the redistribution of hydrogen in the metal structure can be considered as changes in the state of aggregation of the “lattice element”.

The transition of a gas state into a liquid corresponds to the decomposition of a solid solution with a low hydrogen content (α -phase) into two disordered solutions with a lower hydrogen content and a rich hydrogen content. This region is characterized by the appearance of plateau sections on the “pressure-composition” isotherms, corresponding to the Van der Waals isotherms for real gases.

A lattice gas exists at relatively low hydrogen concentrations and high temperatures, and a hydride is a disordered interstitial solution, in which small hydrogen atoms are located at interstices in the metal lattice.

Palladium hydride has a face-centered cubic matrix lattice structure. In the process of absorption of protium and deuterium, the interstitial atoms occupy part of the octahedral interstices. When binary hydrides are formed, the mutual arrangement of metal atoms changes. This is due to the expansion of the crystal lattice. In this case, the structure of the original metal matrix is preserved.

Let us consider the simplest case of uniform deformation (dilatation), i.e., an increase in volume during the sorption of hydrogen with an increase in its concentration $c = N_H/N_M$. (N_M is the number of sites in the metal matrix. N_H is the number of interstitial sites occupied by hydrogen atoms). The dilation coefficient α is a characteristic of the Me–H system and is determined, as a rule,

experimentally. The expansion coefficient of the MH lattice upon dissolution of hydrogen $\alpha = c^{-1}(\Delta V(c)/V)$ is defined as an increase in volume relative to the volume V_0 of the “pure” matrix ($c = 0$).

For hydrogen $\alpha \sim 0.1 \dots 0.2$. Considering that the expansion of the palladium lattice upon dissolution of deuterium in it is about 5% greater than the expansion caused by hydrogen, we take $\alpha_D = 1,05\alpha_H = 0,20$, which gives for the combination $\alpha_{cs} = 0.12$ [4].

The study of interphase processes is reduced to the study of the intermolecular interactions nature, which is the driving force of phase transitions.

When modeling phase transitions in the hydrogen subsystem of MH and describing the molecular phase H_2 in equilibrium with hydride, a unified scheme of the modified perturbation theory (MPT) was used [5].

Phase transformations in metal hydrides are determined by intermolecular interactions.

The main contributions to the (H-H) -interaction for MH are:

- direct (chemical and dispersive) interaction of hydrogen atoms;
- elastic binding energy arising from the deformation of the lattice when hydrogen is introduced into the matrix. This binding energy corresponds to an indirect long-range interaction carried out through the distortion fields of the metal crystal lattice.

The direct interatomic interaction of X -atoms ($X = H, D$) for the hydrogen subsystem of metal hydrides is taken into account by introducing the potential $u_X(r) = kE_1\varphi(r/\sigma_1)$. The parameters of the potential ($X - X$) -interaction: E_1 [K] ($E_1 = \varepsilon_1/k$, ε_1 – the depth of the potential well) and σ_1 [m] (collision diameter), k is Boltzmann's constant. The $E_1\sigma_1^3$ combinations, which are responsible for the energy of the mutual atom – atomic attraction of protium and deuterium, are in the approximate ratio $(E_1\sigma_1^3)_D = 0,97(E_1\sigma_1^3)_H$ [4]. We used the Lennard-Jones pair potential.

Isotope Effect

The isotope effect characterizes the differences in the pressures of hydrogen isotopes on the plateau of equivalent solubility isotherms in the two-phase region $\alpha + \beta$. This is what determines the possibility of using metal hydride working bodies in isotope separation, hydrogen purification and enrichment systems.

Within the framework of the proposed model of a nonideal (interacting) lattice gas of atoms of hydrogen isotopes, the isotope effect of the $PdH_x(D_x)$ system is studied, i.e. the ratio of the equilibrium decomposition pressures of the β -phases of deuteride and hydride $P_{D_2}^{(PL)} / P_{H_2}^{(PL)}$.

The temperature dependences $p_{X_2}^{(PL)}(T)$ of the decomposition pressure of hydride (deuteride) β -phases, that is, the pressure of hydrogen isotopes on the “plateau” of isotherms $p_{X_2}(C)$ in the heterogeneous phase region ($\alpha + \beta$), can be presented in the traditional Van't Hoff form:

$$\ln p_{X_2}^{(PL)}(T) = -\frac{\Delta H_{\beta \rightarrow \alpha}^{(X)}}{RT} + \frac{\Delta S_{\beta \rightarrow \alpha}^{(X)}}{R}, \quad (1)$$

where $X = H, D$; $\Delta H_{\beta \rightarrow \alpha}^{(X)}$, $\Delta S_{\beta \rightarrow \alpha}^{(X)}$ correspond to the enthalpy and entropy of decomposition of the β -phases. These parameters in the MPT circuit are as follows:

$$\Delta H_{\beta \rightarrow \alpha}^{(X)} \cong H_{X_2}^0 + 2RT\Delta_{\beta \rightarrow \alpha}, \quad \Delta S_{\beta \rightarrow \alpha}^{(X)} \cong S_{X_2}^0 - 2R\Delta_{\beta \rightarrow \alpha},$$

where $H_{X_2}^0$, $S_{X_2}^0$ – are the enthalpy and entropy of H_2 (D_2) in the standard state of an ideal gas [6]; the value $\Delta_{\beta \rightarrow \alpha}$ corresponds to the relative difference in the specific enthalpy h_X of the lattice X -gas $h_X^{(i)}(T) \equiv h_X^{st}(T) + h_X^+(\theta_i, T)$ at the boundaries of the homogeneous phases $\theta_\alpha(T)$, $\theta_\beta(T)$.

$$\Delta_{\beta \rightarrow \alpha}(T) = \beta(h_X^{(\alpha)} - h_X^{(\beta)}) / (\theta_\beta - \theta_\alpha) = \beta(h_X^{+(\alpha)} - h_X^{+(\beta)}) / (\theta_\beta - \theta_\alpha) .$$

The boundaries of the α - and β - phases of Pd-H and Pd-D in the temperature range $0^\circ\text{C} \dots t_c^{(H,D)}$ determine the length of the two-phase ($\alpha+\beta$)-region.

The relative concentration of hydrogen in the hydride $\theta=c/c_s$ is the degree of filling of the interstices available for the insertion of X-atoms, c – is the concentration of H(D) in the form of the atomic ratio H(D)/Me, c_s – is the sorption capacity of the metal (maximum value of c).

In equation (1) we use the procedure of averaging in the working temperature range for Pd-D $0^\circ \dots 280^\circ\text{C}$ the values of the enthalpy and entropy of β -phase decomposition.

For protium:

$$\overline{\Delta H}_{\beta \rightarrow \alpha}^{(H)} = H_{H_2}^0(\bar{t}) + 2R\bar{T}\Delta_{\beta \rightarrow \alpha}^{(H)} ; \quad \overline{\Delta S}_{\beta \rightarrow \alpha}^{(H)} = S_{H_2}^0(\bar{t}) - 2R\Delta_{\beta \rightarrow \alpha}^{(H)} .$$

At $\bar{t} = 140^\circ$, according to [5] $H_{H_2}^0(\bar{t}) = 13,04$ kJ/mol H_2 , $S_{H_2}^0(\bar{t}) = 139,8$ J/(K·mol H_2), which gives $\overline{\Delta H}_{\beta \rightarrow \alpha}^{(H)} = 40,51$ kJ/mol H_2 , $\overline{\Delta S}_{\beta \rightarrow \alpha}^{(H)} = 96,34$ J/(K·mol H_2).

For deuterium:

$$\overline{\Delta H}_{\beta \rightarrow \alpha}^{(D)} = H_{D_2}^0(\bar{t}) + 2R\bar{T}\Delta_{\beta \rightarrow \alpha}^{(D)} ; \quad \overline{\Delta S}_{\beta \rightarrow \alpha}^{(D)} = S_{D_2}^0(\bar{t}) - 2R\Delta_{\beta \rightarrow \alpha}^{(D)} .$$

At $\bar{t} = 140^\circ$, according to [5] $H_{D_2}^0(\bar{t}) = 11,930$ kJ/mol D_2 , $S_{D_2}^0(\bar{t}) = 154,29$ J/(K·mol D_2), which gives $\overline{\Delta H}_{\beta \rightarrow \alpha}^{(D)} = 36,11$ kJ/mol D_2 , $\overline{\Delta S}_{\beta \rightarrow \alpha}^{(D)} = 95,76$ J/(K·mol D_2).

Branches $C_i(T) = C_s \cdot \theta_i(T)$ (dependences $\theta_\alpha(T)$, $\theta_\beta(T)$) of the homogeneous phases decomposition curves of Me-X systems into disordered phases $i = \alpha, \beta$ are determined by the equilibrium conditions

$$\begin{cases} p_X(\theta_\alpha, T) = p_X(\theta_\beta, T); \\ \mu_X^+(\theta_\alpha, T) = \mu_X^+(\theta_\beta, T), \end{cases} \quad (2)$$

where $p_X(\theta, T)$ – is the pressure of the X-lattice gas can be represented as [7]

$$\frac{1}{T} p_X(\theta, T) = \frac{kc_s}{\Omega} \left[-\frac{\ln(1-\theta)}{1+\alpha c_s \theta} + \frac{W_1/2}{T} \left(\frac{\theta}{1+\alpha c_s \theta} \right)^2 + \frac{2W_2/3}{T^2} \left(\frac{\theta}{1+\alpha c_s \theta} \right)^3 \right],$$

where $\Omega = v_0 / n_M$ – is the specific volume of the matrix at $c = 0$ (v_0 – is the volume of the unit cell of the "pure" metal, i.e., at $c = 0$; n_M – is the number of metal atoms per cell); $\alpha = \omega / \Omega$ – dilatation coefficient (ω – increase in the lattice volume upon the introduction of one H atom).

Dependence of the "excess" chemical potential of dissolved atoms of isotopes on the concentration and temperature in the region of disordered α - and β – phases of Pd-H and Pd-D [8]

$$\beta \mu_X^+(\theta, T) = \ln \frac{\theta}{1-\theta} + \frac{W_1 \theta}{T(1+\alpha c_s \theta)} + \frac{W_2 \theta^2}{T^2(1+\alpha c_s \theta)^2} ,$$

where $\beta=1/kT$; $\mu_X^+ = \mu_X - \mu_X^{st}$; $\mu_X^{st}(T)$ – chemical potential in standard state.

Constants W_1 and W_2 are equal:

$$W_1 = 2I_1 n_M (\sigma_1^3 / v_0) E_1 c_s, \quad W_2 = (3I_2 / 4I_1^2) W_1^2,$$

where $I_1 = -5,585$, $I_2 = 1,262$ – MPT parameters for H(D)–gas [5]. The constants W_1 and W_2 provide a connection between the macroscopic characteristics of interstitial solutions of hydrogen MH–isotopes and the microscopic (atomic) characteristics of the hydrogen subsystem and the metal matrix of MH. For the Pd–D system, when determining the parameters W_1 and W_2 , the values $n_M = 4$ (FCC – lattice, O – interstices), $c_s = 0.6$, and, of course, v_0 are the same as for Pd–H.

Fig.1 shows the boundaries of the regions of disordered phases (CT- decomposition curves) of the Pd–H and Pd–D systems, calculated from the equilibrium conditions for the α - and β -phases (2).

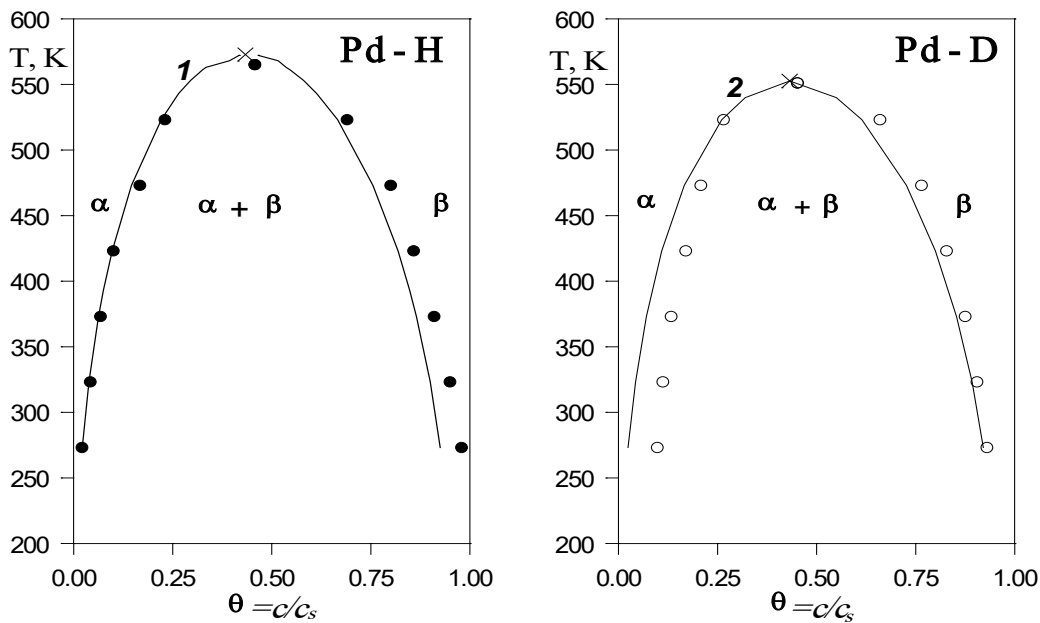


Fig. 1. Curves of decomposition of homogeneous phases of palladium hydride and deuteride into disordered α - and β - phases: 1,2 calculation, symbols - experiment [9].

Let us consider the differences in the phase equilibria of palladium with two hydrogen isotopes - protium H and deuterium D, i.e. for PdH_x hydride and PdD_x deuteride.

Table 1. Results of modeling the phase diagrams of Pd–H and P–D in the region of α – β –equilibria.

$t, ^\circ C$	$\theta_\alpha=c_\alpha/c_s$ (Pd–H)	$\theta_\beta=c_\beta/c_s$ (Pd–H)	P_{H_2}, atm (1)	$\theta_\alpha=c_\alpha/c_s$ (Pd–D)	$\theta_\beta=c_\beta/c_s$ (Pd–D)	P_{D_2}, atm (1)
0	0.02163	0.9253	0.00193	0.02430	0.92077	0.0125
50	0.03837	0.9004	0.0305	0.04307	0.89258	0.1461
100	0.06264	0.8653	0.2301	0.07039	0.85312	0.8848
150	0.097	0.8184	1.076	0.10935	0.79993	3.500
200	0.1456	0.7552	3.633	0.16625	0.72695	10.35
241,09				0.20353	0.6837	8.271
250	0.2207	0.6657	9.719	0.26086	0.61454	24.90

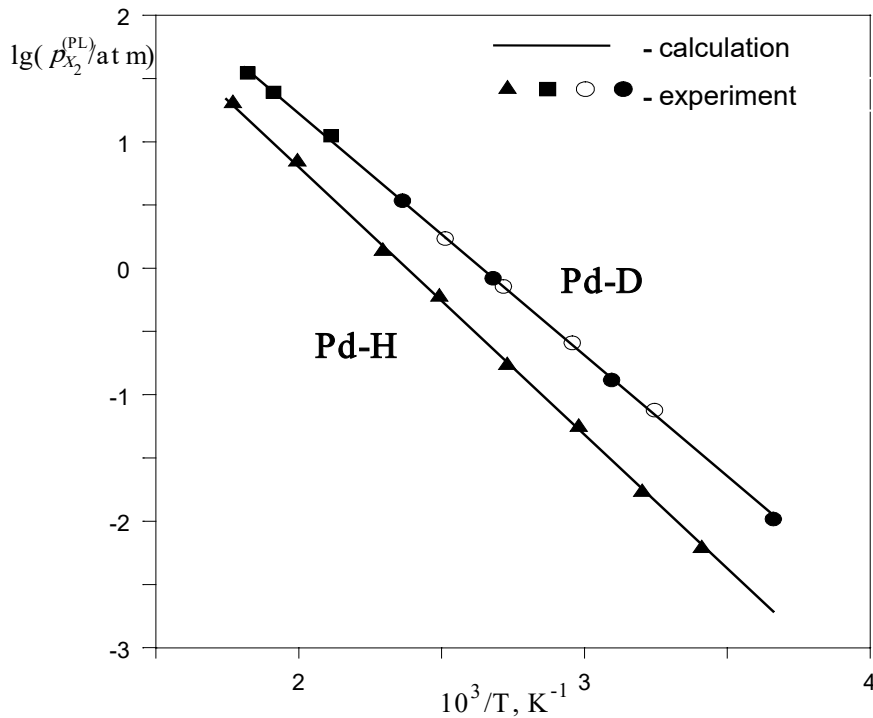


Fig. 2. Logarithm of the decomposition pressure of the β -phase of the Pd-H and Pd-D systems as a function of return temperature

According to (1), for the ratio of the equilibrium decomposition pressures of the β -phases of deuteride and hydride, we obtain:

$$\ln(P_{D_2}^{(PL)} / P_{H_2}^{(PL)}) = -\frac{\delta(\Delta H_{\beta \rightarrow \alpha})^{D-H}}{RT} + \frac{\delta(\Delta S_{\beta \rightarrow \alpha})^{D-H}}{R},$$

where $\delta(\Delta A_{\beta \rightarrow \alpha})^{D-H} = \Delta A_{\beta \rightarrow \alpha}^{(D)} - \Delta A_{\beta \rightarrow \alpha}^{(H)}$ – is the difference between the thermodynamic parameters of the decomposition of the β -phases of Pd-D and Pd-H.

Using the above averaged parameters of hydride phases $\overline{\Delta H_{\beta \rightarrow \alpha}}^{(D)} = 36,11$ kJ/mol D_2 , $\overline{\Delta S_{\beta \rightarrow \alpha}}^{(D)} = 95,76$ J/(K·mol D_2) and $\overline{\Delta H_{\beta \rightarrow \alpha}}^{(H)} = 40,51$ kJ/mol H_2 , $\overline{\Delta S_{\beta \rightarrow \alpha}}^{(H)} = 96,34$ J/(K·mol H_2), we can obtain a simple equation for the ratio:

$$P_{D_2}^{(PL)} / P_{H_2}^{(PL)} = \exp\left(\frac{528,7}{T} - 0,07\right).$$

For the Pd- $H_2(D_2)$ system, the opposite isotope effect is observed. The pressure of hydrogen isotopes on the "plateau" of equivalent solubility isotherms of the heavier D_2 isotope is greater than that of H_2 . The nature of the inverse isotope effect is mainly determined by the lower energy of the (D-D)-interaction in the lattice as compared to the (H-H)-interaction. On the other hand, an important factor is the difference in the energies of zero point vibrations of protium and deuterium atoms in the metal lattice.

Conclusions

The behavior of hydrogen isotopes absorbed by the transition metal palladium is analyzed. A mathematical model of the lattice gas of sorbed atoms has been developed, which considers the interaction between them and takes into account the increase in the volume of the crystal lattice. In this case, the crystal structure of the metal does not change. This made it possible to describe the

isotope effect observed during the dissolution of protium and deuterium. The calculated characteristics of metal hydrides and deuterides can be used in the design of hydrogen isotope separation devices.

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