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Thermodynamic optimization of the system magnesium–hydrogen[☆]

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Abstract

On the basis of our own calorimetric data and of known equilibria data the phase equilibria in the system Mg–H have been completely calculated by means of an optimization. Both for α-MgH_x and MgH_2 optimized free enthalpy functions are obtained.

Keywords: Magnesium hydride; Enthalpy of formation; Entropy of formation

1. Introduction

Because of its high hydrogen content of 7.7 wt% and due to enthalpy changes resulting from formation and decomposition respectively, magnesium hydride MgH_2 is interesting both as hydrogen absorbent and heat absorbent at medium temperatures. Accordingly, there is a large number of published results covering the formation and decomposition equilibria presented by the known pressure/composition isotherms [1–10,14,15]. The thermodynamic evaluation of these experimental results is usually based upon the van't Hoff equation. Thus, values for the enthalpy of formation $\Delta_f H$ and for the entropy of formation $\Delta_f S$ are resulting.

A comparison between the $\Delta_f H$ and $\Delta_f S$ values by different authors indicates considerable deviations (about 7%), which are still magnified, if equilibria pressures are concerned. These considerable differences are caused by the following, frequently unconsidered factors: very slow adjustment of equilibrium, temperature dependence of $\Delta_f H$ and $\Delta_f S$, hysteresis between pressure of formation and pressure of decomposition, the real behaviour of gaseous hydrogen and the solubility of hydrogen in magnesium (α-MgH_x, $0 < x < 0.1$).

In this paper it is presented that on the basis of different experimental data an optimized record for the thermodynamic description of both the phase and the reaction equilibria can be obtained. The experimental data [2,4,8,9] are derived from equilibrium measurements and from calorimetric measurements of our own [11,12].

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2. Basic data

Experimental investigations on the thermodynamic properties of the system Mg–H nearly exclusively are based upon the measurement of equilibrium pressures as a function of temperature. In Table 1 values of enthalpy of formation and entropy of formation, derived from those measurements, are given. The considerable scattering of the values does not allow the derivation of optimized values on that basis. Only in a few cases the original measured values ($p = f(T)$) are reported [2,4,8,9].

On the basis of heat capacity measurements by means of adiabatic low temperature calorimetry within the temperature range from 15 to 300 K [11] and DSC within the temperature range from 290 to 360 K we determined the molar standard entropy and the temperature behaviour of heat capacity $C_p(T)$ within the range 15–360 K for magnesium hydride. In addition, the enthalpy of desorption at 683 K for the reaction:

$$\mathrm{MgH_2} \Rightarrow \mathrm{Mg} + \mathrm{H_2(g)}$$

could be determined [12]. Out of 14 desorption measurements a mean value of

$$\Delta_{\mathrm{R}} H^0_{\mathrm{MgH_2}} = (74.05 \pm 1.3)\,\mathrm{kJ/mol\,H_2}$$

is calculated.

By the use of these values the thermodynamic reaction behaviour can be completely calculated under the assumption, that the enthalpy of formation and that of decomposition are identical. From the values presented in the table for hydrogen and magnesium [13]:

$$S^0_{\mathrm{Mg}}(298\,\mathrm{K}) = 32.677\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$S^0_{\mathrm{Mg}}(298\,\mathrm{K}) = 130.679\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\begin{aligned} C_{p_{\mathrm{Mg}}}(T) = \big(&26.185 - 9.716\times 10^{-4}\,T\ (\mathrm{K}) \\ &+ 8.362\times 10^{-6}\,T^2\ (\mathrm{K}^2) - 1.579 \\ &\times 10^5\,T^{-2}\ (\mathrm{K}^{-2})\big)\,\mathrm{J\,K^{-1}\,mol^{-1}}, \end{aligned}$$

$$\begin{aligned} C_{p_{\mathrm{H_2}}}(T) = \big(&31.3571 - 0.005518\,T\ (\mathrm{K}) \\ &+ 4.4783\times 10^{-6}\,T^2\ (\mathrm{K}^2) - 1.1317 \\ &\times 10^5\,T^{-2}\ (\mathrm{K}^{-2})\big)\,\mathrm{J\,K^{-1}\,mol^{-1}}, \end{aligned}$$

the following equations are obtained for the reaction of formation:

$$\mathrm{Mg} + \mathrm{H_2} \rightarrow \mathrm{MgH_2} \tag{1}$$

$$\begin{aligned} \Delta_{\mathrm{f}} C_p = \big(&-54.671 + 0.1171\,T\ (\mathrm{K}) - 1.284 \\ &\times 10^{-5}\,T^2\ (\mathrm{K}^2) + 3.39676 \\ &\times 10^5\,T^{-2}\ (\mathrm{K}^{-2})\big)\,\mathrm{J\,K^{-1}\,mol^{-1}}, \end{aligned} \tag{2}$$

$$\Delta_{\mathrm{f}} H^0_{\mathrm{MgH_2}}(298\,\mathrm{K}) = \Delta_{\mathrm{f}} H^0_{\mathrm{MgH_2}}(683\,\mathrm{K}) - \int_{298}^{683} \Delta_{\mathrm{f}} C_p \,\mathrm{d}T,$$

$$\Delta_{\mathrm{f}} H^0_{\mathrm{MgH_2}}(298\,\mathrm{K}) = -74.513\,\mathrm{kJ\,mol^{-1}\,H_2},$$

$$\begin{aligned} \Delta_{\mathrm{f}} H^0_{\mathrm{MgH_2}}(T) = (&-74513 - 54.67(T - 298) \\ &+ 0.0586(T^2 - 298^2) - 4.28 \\ &\times 10^{-5}(T^3 - 298^3) - 3.396 \\ &\times 10^5(T^{-1} - 298^{-1}))\,\mathrm{kJ\,mol^{-1}\,H_2}, \end{aligned} \tag{3}$$

$$\begin{aligned} \Delta_{\mathrm{f}} S^0_{\mathrm{MgH_2}}(T) = (&-132.72 - 54.67\ln(T/298) \\ &+ 0.117(T - 298) - 6.42 \\ &\times 10^{-6}(T^2 - 298^2) - 1.70 \\ &\times 10^5(T^{-2} - 298^{-2}))\,\mathrm{J\,K^{-1}\,mol^{-1}\,H_2}. \end{aligned} \tag{4}$$

Table 1
Enthalpies and entropies of formation for MgH_2

$\Delta_f H$ (exp) kJ mol^{-1}	$\Delta_f S$ (exp) J K^{-1} mol^{-1}	Temperature range (°C)	Reference
−74.0		380–480	[1]
−73.1	−135.8	440–560	[3]
−74.1		234–278	[4]
−77.4	−138.3	300–350	[5]
−85.0	−137.0	280–360	[6]
−70.1	−126.0	303–390	[2]
−74.3	−136.0	280–370	[7]
−80.9	−144.8	300–450	[8]
−81.2	−146.1	270–345	[9]
−74.7	−135.3	320–480	[10]

By means of $\ln f = -(\Delta_f H^0/RT) + (\Delta_f S^0/R)$ the following function for equilibrium fugacity in bar is obtained

$$\ln(f/bar) = -7477.09\,T^{-1} - 24.1781 + 6.57578\ln T - 7.0423\times10^{-3}\,T + 2.574\times10^{-7}\,T^2 - 20427.94\,T^{-2}. \quad (5)$$

This relationship is first of all an approximation, since the solubility of hydrogen in magnesium is not considered. This solubility increases with temperature. This fact is connected with the systematic deviations, which are increasingly observed between calculated (Eq. (5)) and experimentally determined equilibrium fugacity. Therefore it is absolutely necessary to include solubility into the thermodynamic modelling of the system Mg–H.

3. Thermodynamic optimization

3.1. Fundamentals

The thermodynamic calculation of complex equilibria is based upon the minimization of free enthalpy:

$$G = \sum n_i \mu_i. \quad (6)$$

We used an extensive computer program ChemSage [16]. The minimization of the free enthalpy of the system as a whole is only possible, if also for the integral free enthalpy G_m of included mixing phases an analytical expression will be available. As for other metal–hydrogen systems successfully applied, the WAGNER model has been used for the mixing phase α-MgH$_x$:

$$G_m = \sum_{i=1}^{2} \mu_i^0 + RT\sum_{i=1}^{2} x_i \ln x_i + x_1 RT \ln\gamma_1 + x_2 RT(\ln\gamma_1 + \ln\gamma_2^0 + \varepsilon_{12}x_2), \quad (7)$$

where x_i is the mole fraction of the component i; μ_1^0 is the standard potential of magnesium; μ_2^0 is the standard potential of the solved hydrogen; γ_1 is the activity coefficient of magnesium; γ_2^0 is the activity coefficient of hydrogen ($x_2 = 0$); ϵ_{12} is the parameter of interaction.

The required consideration of the real behaviour of the gaseous hydrogen has been made in the most simple form:

$$f = \phi\times p;\quad \ln(\phi) = B(T)p/RT;\quad B(T) = \alpha - \beta/RT, \quad (8)$$

where ϕ is the fugacity coefficient; $B(T)$ is the second virial coefficient.

The constants α and β have been calculated from the known temperature dependence $B(T)$ [17]:

$$\alpha = 22.34\,\mathrm{cm^3\,mol^{-1}};\quad \beta/R = 2430.8\,\mathrm{cm^3\,K\,mol^{-1}}.$$

3.2. Optimization

An optimization routine has recently been implemented into the ChemSage program [18], which allows the use of independent experimental data for the determination and optimization of selected thermodynamic parameters of the free standard enthalpy and of excess enthalpy. The non-linear error square procedure is based upon the Bayes algorithm. The error function $E(p)$, which is to be minimized with respect to the vector of model parameters p, consists of two terms: (1) the difference between the predicted and experimental data; (2) the difference between estimated and a priori parameters:

$$E(p) = [f(p) - y]^{\mathrm{T}} C_y^{-1}[f(p) - y] + [p - p^0]^{\mathrm{T}} C_{p^0}^{-1}[p - p^0], \quad (9)$$

p^0, y and $f(p)$ are vectors of the priori parameters, of experimental data and the values calculated. C_y and C_{p^0} are covariant matrices of the experimental values y and of the priori parameter p_0. Both terms of equation allow a different evaluation of the input data y and p_0. Thus, also independent experimental data can be estimated differently as regards their error.

3.3. Experimental data and parameters

The following experimental data were used for optimization

Equilibrium pressures of MgH$_2$ by four authors [2,4,8,9]. These data have been transformed, according to Eq. (7), into the fugacities, from

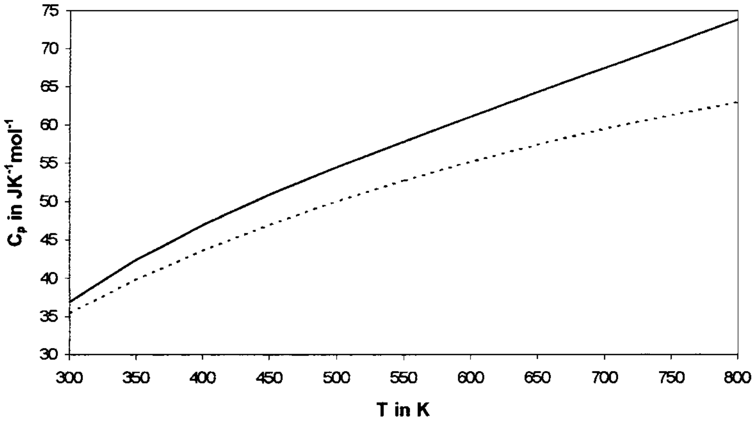

Fig. 1. Molar heat capacity of MgH_2: (—) this work; (—) [13].

which by use of a polynomial (see Eq. (5)) mean values were found.

Saturation concentration of hydrogen in α-MgH_x [2] in the temperature range from 700 to 800 K.

Heat capacity values in the temperature range from 100 to 360 K (measurements of our own).

Desorption enthalpy at 683 K (DSC measurements of our own).

Parameters to be achieved were:

Heat capacity function $C_p(T) = a + bT + cT^2 + dT^{-2}$ for MgH_2 in the temperature range from 100 to 850 K.

Standard enthalpy of formation $\Delta_f H^0$ (298) for MgH_2.

Free excess enthalpy for α-MgH_x.

4. Results of optimization

The result of optimization shows that all the experimental data are recorded within their error limits. For the stoichiometric magnesium hydride MgH_2 the following results are obtained:

4.1. Standard enthalpy of formation

$$\Delta_f H^0_{298.15} = -74.70\,\mathrm{kJ\,mol^{-1}}.$$

This is in good accordance with the value of $-74.4 \pm 0.9\,\mathrm{kJ\,mol^{-1}}$, reported by Stampfer et al. [2], the only tabulated and too a high value of $-76.15\,\mathrm{kJ\,mol^{-1}}$ [13] has been derived by unweighted averaging.

4.2. Molar heat capacity

$$C_p = (35.62 + 0.0401 \times T + 1.215 \times 10^6 \times T^{-2})\,\mathrm{J\,K^{-1}\,mol^{-1}}.$$

Fig. 1 presents the temperature dependence in comparison with the tabulated values. All the tabulated values are referred to an estimation, such that the heat capacity of MgH_2 and MgF_2 should have the similar temperature behaviour.

4.3. α-Magnesium hydride

The experimental values for α-MgH_x can be sufficiently described by the model of the ideal solution. For equilibrium fugacity H_2 results:

$$\ln\left(\frac{f_{H_2}^{1/2}}{bar^{1/2}}\right) = \frac{1609.9}{T\ (\mathrm{K})} + 3.649 + \ln(x_H). \quad (10)$$

From this relationship the well-known Sievert law can be derived for a given temperature:

$$x_H = \mathrm{Const}(T) \times p_{H_2}^{1/2},$$

$$\mathrm{Const}(T) = \exp\left(-\frac{\Delta_L H^0_\infty}{RT} + \frac{\Delta_L S^0_\infty}{R}\right),$$

Solution enthalpy of hydrogen :

$$\Delta_L H^0_\infty = 13.38\,\mathrm{kJ\,mol^{-1}\,H},$$

Solution entropy of hydrogen :

$$\Delta_L S^0_\infty = -30.33\,\mathrm{JK^{-1}mol^{-1}\,H}.$$

The value of the solution entropy lies within the range, as it is known for metal–hydrogen systems. The positive solution enthalpy is in accordance with the estimations on the basis of semi-empirical models.

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