Characterization of hydrogen storage materials by means of pressure concentration isotherms based on the mass flow method

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The determination of the equilibrium thermodynamic parameters of hydrogen storage materials from quasiequilibrium pressure data using the mass flow pressure concentration isotherm (pcI) method is presented. The method bases on the acquisition of pcI curves at different flow rates using a thermal mass flow controller to determine the amount of ad/desorbed hydrogen. These measurements provide a set of corresponding quasiequilibrium pressure functions from, which the true equilibrium pressure of the hydride is calculated by extrapolation to zero flow. The governing thermodynamic parameters can then be determined to characterize the material by the construction of a van't Hoff plot, extracting enthalpy of reaction ΔH_r and entropy of reaction ΔS_r from the equilibrium pressure p_{eq} as a function of temperature. Naturally, true equilibrium can never be reached and therefore can only be approximated by measurement—a drawback that all experimental techniques share. This complication is alleviated by the flow-pcI approach at different flow rates. The compilation of the $p_{eq}(T)$ data from pcI-measurements can be performed by different methods, whereas the so called Sieverts apparatus is most commonly used. In this paper, we elaborate the differences and advantages of the mass flow-pcI over the Sieverts Apparatus and present measurements and results on LaNi_5 as a benchmark. Measurements at different flow rates are presented and equilibrium pressures at zero flow are achieved by extrapolation. The obtained results of $\Delta H_d = 32.5 \text{ kJ mol}^{-1} \text{ H}_2$ and $\Delta S_d = 115 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$ (desorption process) perfectly match literature values, emphasizing the excellent quality of the measurements and the performance of this measurement apparatus. © 2009 American Institute of Physics. [DOI: 10.1063/1.3186731]

I. INTRODUCTION

On the verge of limited hydrocarbon supplies and anthropogenic climate change, alternative energy carrier solutions are moving into focus. Hydrogen as an energy carrier is debated in this context. While hydrogen so far is the only artificial energy carrier that can be produced in real time to satisfy our energy needs, the storage problem is still not solved satisfactory.^{1,2} Especially for mobile applications, where autonomy, refuelling times and energy efficiency are considered crucial factors, the challenges remain considerable.

Solid hydrogen storage has been greatly studied for so called metal hydrides. While these materials offer high volumetric hydrogen storage densities, the gravimetric storage density is low due to the high specific mass of the materials involved. Recently, the focus of interest shifted toward complex hydrides due to their much higher gravimetric storage density.³ While the mechanism of hydride formation, synthesis and desorption are completely different, the requirements to put them in use as solid hydrogen storage materials remain the same: stability and kinetics must lie in a suitable range for application. These parameters can be influenced by suit-

able substitutions and additions of catalysts.^{4–7} The study of the thermodynamic properties therefore gives us a key for understanding the underlying processes.

The thermodynamic aspects of hydride formation from gaseous hydrogen are described by means of pressure concentration isotherms (pcIs). (For complete discussions about the underlying physical phenomena of hydride formation, the interested reader is referred to more specific literature.^{1,8}) In a typical intermetallic compound, there exists a plateau region of phase coexistence between the solid solution (α -phase) and the hydride phase (β -phase). The length of this plateau region determines the amount of hydrogen stored and the center of the plateau is generally referred to as the equilibrium pressure. The equilibrium pressure p_{eq} is related to changes of enthalpy of reaction ΔH_r and entropy of reaction ΔS_r by the van't Hoff equation

$$\ln\left(\frac{p_{eq}}{p_0}\right) = \frac{\Delta H_r}{R} \frac{1}{T} - \frac{\Delta S_r}{R}, \quad (1)$$

with $p_0 = 1.013 \times 10^5 \text{ Pa}$ and R is the ideal gas constant. As can be seen from this relationship, the thermodynamic parameters can be found by the equilibrium pressures at a given temperature—hence the name pcI. The aim of this paper is to present a new method of acquiring pcI-data and the thermodynamic properties of a hydrogen storage material. Hereafter, the classical method by the so called Sieverts Ap-

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FIG. 1. Schematic setup of (a) Sieverts type apparatus for pCI-measurements and (b) flow-pCI setup. The top shows the general flow path for adsorption measurements, while the bottom graph shows the setup for desorption measurements.

paratus is discussed followed by the description of the proposed mass flow-pCI method.

II. DESCRIPTION OF THE SIEVERTS APPARATUS

Subsequently, the general concept of the Sieverts-Apparatus is described. The basic concept of measurement and the construction of the van't Hoff plot from these measurements are described along with the fundamental limitations and problems of the technique. The general concept of the Sieverts apparatus is schematically represented in Fig. 1 and compared to the flow-pCI apparatus. The system consists of the following components:

- H₂ gas supply with pressure regulator,
- reference volume (thermally stabilized) with temperature measurement,
- pressure measurement,
- temperature controlled sample container, and
- vacuum supply.

The general measurement procedure follows an iterative process. To determine the adsorption pCI-curve, a carefully prepared sample (evacuation, activation, conditioning, heating to desired temperature and stabilization of conditions) is separated from the reference volume and the later is filled with hydrogen at a pressure of $p_i = i \cdot \Delta p_{\text{inc}}$ with Δp_{inc} being a carefully chosen pressure increment.⁹ As the supply and the reference volume generally are at different temperatures, a suitable stabilization time is required to let the gas heat to the well defined temperature T_{case} . The sample is then connected and the gas expands from the reference volume V_{ref} into the combined volume $V_{\text{ref}} + V_{\text{holder}} - V_{\text{sample}}$. After a suitable stabilization time $t_{r,i}$ the sample has reached equilibrium and the pressure stabilizes at $p_{\text{eq},i} = p_i - \Delta p_i$. The sample is then again disconnected from the reference volume and the process is repeated at $p_{i+1} = (i+1) \cdot \Delta p_{\text{inc}}$ until the desired final pressure is reached. The collected data set $p_{\text{eq},i}$, p_i and V_{ref} serve as a basis to calculate the amount of hydrogen adsorbed by using the system constants and sample mass m_{sample} . The pressure evolution is schematically represented in Fig. 2. The amount of hydrogen molecules absorbed Δn_i in the material in the i th step can be calculated according to

FIG. 2. Schematics of the measurement procedure in a Sieverts apparatus. The schematics illustrates the acquisition of point $i+1$.

$$\Delta n_i = \Delta n_{\text{ref},i} - \Delta n_{\text{holder}} = \left(\frac{p_i}{Z \cdot R \cdot T_{\text{ref}}} - \frac{p_{\text{eq},i}}{Z \cdot R \cdot T_{\text{ref}}} \right) V_{\text{ref}} - \left(\frac{p_{\text{eq},i}}{Z \cdot R \cdot T_{\text{sample}}} - \frac{p_{\text{eq},i-1}}{Z \cdot R \cdot T_{\text{sample}}} \right) (V_{\text{holder}} - V_{\text{sample}}), \quad (2)$$

whereas Z is the Z -compressibility factor at the respective pressures and temperatures (indices omitted for simplicity). Note that V_{sample} comprises the volume displaced by the adsorbing material and is dependent on the amount of hydrogen adsorbed which is actually the information we seek from this experiment. If this error is significant or not strongly depends on $\{V_{\text{ref}}, V_{\text{holder}}, V_{\text{sample}}, \partial p_i\}$ and errors of up to 100% might arise if no care is taken.⁹ The total amount of hydrogen adsorbed in the n th step is given by

$$n_i = \sum_k \Delta n_k. \quad (3)$$

It is worthwhile to mention, that the stabilization time $t_{r,i}$ depends strongly on the kinetics of the material and thermal transport properties of the setup. Desorption is measured analogous by applying pressure decrements $p_i = i \cdot \Delta p_{\text{dec}}$.

While the Sieverts method offers a rather simple setup and can be implemented in various degrees of complexity, it has some mayor inconveniences.

- The error on n_i is the sum of all errors on Δn_i .
- $p_i = i \cdot \Delta p_{\text{inc}}$ is by default different than the equilibrium pressure $p_{\text{eq},i}$ the system will relax to in the i th step.
- In samples with slow kinetics, equilibrium is never reached in experimentally acceptable time frames.
- A small Δp_{inc} will keep the sample close to its equilibrium state $p_{\text{eq},i}$ and reduce stabilization time, but the corresponding error on n_i will increase due to pressure measurement precision limitations and vice versa.
- Δp_{inc} must be chosen to give a point density to determine the pCI-curve with sufficient precision to determine the plateau.

Data acquisition and treatment is tedious and a rather complex task. Additionally, slow measurements (kinetically slow materials) impose more stringent constraints on system tightness which has to be negligible during a set of absorption and desorption measurements. The sequential data acquisition leads to system leakage over time due to valve wear

as each measurement point involves valve actuation. While the acquisition can be automated by using actuated valves, this usually comes at the cost of system tightness. Most automatic valves have a well defined flow direction due to design, using a spring acting as a counterforce. Therefore, they offer by design not the same tightness in both flow directions.

III. DESCRIPTION OF THE MASS FLOW-PCI APPARATUS

In this chapter, we elaborate the measurement principle of pci-measurements with the mass flow method. The concept is based on the direct measurement of supplied hydrogen mass to the sample, sample pressure and temperature. The hydrogen mass flow at standard or normalized conditions (depending on calibration) is determined by means of a thermal mass flow controller (MFC). These MFCs measure the amount of a gas flowing through the device by using the heat capacity of the gas under investigation. The gas is passing through a flow channel and the inlet temperature T_1 is measured. The gas flow passes a heating element R_H and the temperature T_2 at the outlet is determined. The temperature difference thus established is as follows:

$$\Delta T = \alpha \cdot C_p \cdot \rho \cdot \phi_V = \alpha \cdot C_p \cdot \phi_m, \quad (4)$$

whereas α is a constant, C_p is the heat capacity of the gas, ρ is the density, ϕ_V is the volumetric flow, and ϕ_m the gravimetric flow. This concept demands that the gas under investigation is known and sufficiently pure—both restrictions are easily fulfilled for the application in question. An actuated valve at the outlet port is actuated to obtain the desired gas flow through the device. The main advantage of the technique is that the measurement signal ΔT is directly proportional to the gravimetric flow ϕ_m and independent of input gas temperature and pressure, greatly decreasing the necessity for corrections and improving precision. It is worth mentioning, that inlet and outlet pressure are therefore different from each other and the flow at the outlet port at the respective pressure is decoupled from the pressure at the inlet of the MFC, providing conditions remain within operational limits of the device. The specifications of the MFC used in the current setup are $0.1 \text{ SCCM} < f < 3 \text{ SCCM}$ (SCCM = standard cm^3/min), $\Delta p_{\text{input-output}}^{\text{max}} = 40 \text{ bar}$, $p_{\text{input}}^{\text{max}} = 100 \text{ bar}$, precision 1% full scale, and repeatability 0.25% of rate.

The detailed mass flow-pci Apparatus modes of operation are depicted in Fig. 3 for adsorption and desorption measurements. To determine the adsorption characteristics of a hydrogen storage material, a carefully prepared sample (evacuated, stabilized temperature) at temperature T is supplied with a constant flow f of hydrogen from a gas cylinder. The pressure $p(t)$ at the outlet of the MFC is measured continuously as the gas starts to fill the volume V_{dead} containing the sample under investigation at the outlet port of the MFC. The acquisition is performed until the desired p_{final} in the system is reached. From these measurements, $p(t)$, f , and $V_{\text{sup}}(t)$ are collected. $V_{\text{sup}}(t)$ at standard conditions is the volume of hydrogen supplied to the volume $V_{\text{dead}} = V_{\text{system}} + V_{\text{connection}} + V_{\text{holder}}$, as depicted in Fig. 4 and can be calculated by $V_{\text{sup}} = \int f(t) dt$.

FIG. 3. Schematic of the mass flow pci-apparatus setup and the flow concept for (a) adsorption measurements and (b) desorption measurements, which can be selected by choosing the respective flow path through the device. The machine is kept at a stable temperature $T_{\text{case}} = \text{const.}$

The procedure to extract the amount of hydrogen adsorbed in the sample will now be discussed. For desorption measurements, the equivalent acquisition is performed, starting a p_{initial} and letting the hydrogen flow through the MFC into vacuum, while measuring $p(t)$ at the inlet of the MFC. For sake of simplicity, only the adsorption case will be presented.

In Fig. 5 $p(t)$ is represented for the case of a (a) empty sample holder and (b) with a sample present. The amount of hydrogen present in the system can be expressed as

$$n_{\text{sup}}(t) = n_{\text{gas}}(t) + n_{\text{solid}}(t), \quad (5)$$

whereas $n_{\text{sup}}(t)$ is the amount of hydrogen supplied by the MFC, $n_{\text{gas}}(t)$ is the amount of hydrogen in V_{dead} remaining in the gas phase, and $n_{\text{solid}}(t)$ the amount of hydrogen adsorbed in the sample and consequently removed from the gas phase. The amount of hydrogen flowing into the system can be calculated using the ideal gas law

FIG. 4. Description of the different volumes of the mass flow-pci-apparatus. Only the case for the adsorption measurement are shown. The design of the apparatus is such that the desorption case is symmetric. In the current setup, $V_{\text{dead}} = 4.4 \text{ cm}^3$. Only the outside connection tube $V_{\text{connection}}$ is not kept at a stabilized temperature.

FIG. 5. Pressure evolution as a function of supplied H_2 n_{sup} at standard conditions and constant flow with (a) empty sample container (b) sample container with a sample. The pressure difference is due to absorption of hydrogen from the gas phase into the sample. (c) Represents the p as a function of n_{solid} after correction of (b) from (a) according to Eq. (9) in the analytical description.

$$n_{sup}(t) = \frac{p \cdot V_{sup}}{R \cdot T} = \frac{p^* \cdot f \cdot t}{R \cdot T^*}, \quad (6)$$

with $p^* = 1.013$ bars, $T^* = 20$ °C, and R the gas constant as f is measured directly for standard conditions from the MFC.

Assuming an empty sample cylinder [Fig. 5(a)] $n_{solid}(t) = 0$ and therefore all H_2 remains in the gas phase and

$$\begin{aligned} n_{gas}(t) &= \frac{p(t)}{R} \cdot \left(\frac{V_{system}}{T_{case}} + \frac{V_{connection}}{T_{RT}} + \frac{V_{holder}}{T_{sample}} \right) \\ &= \frac{p(t) \cdot V'}{R \cdot T'}, \end{aligned} \quad (7)$$

where V' and T' are apparent system volume and temperature and comprise the volumes and temperatures of all components connected to the MFC's outlet port, while T_{RT} is the room temperature. Using expressions (6) and (7) and assuming an empty sample cylinder we find

$$\frac{dp(t)}{dt} = A \cdot f \quad A = \frac{p^* \cdot T'}{T^* \cdot V'}, \quad (8)$$

where A is constant for a given T_{sample} and therefore can be evaluated empirically from the slope of $dp(t)/dt$ in (a) of Fig. 5 or calculated from the individual subvolumes and temperatures. While T_{RT} is fluctuating due to temperature variations in the laboratory; these contributions are small because $V_{connection} < V_{system}, V_{holder}$. These contributions are included if A is determined empirically.

If a hydrogen adsorbing sample is present [$n_{solid}(t) > 0$] the pressure increase is lowered due to hydrogen absorption by a sample from the gas phase. The amount of hydrogen adsorbed is given by

$$\begin{aligned} n_{solid}(t) &= n_{sup}(t) - n_{gas}(t) = \frac{p^* \cdot f \cdot t}{R \cdot T^*} - \frac{p(t) \cdot V'}{R \cdot T'} \\ &= \frac{p^*}{R \cdot T^*} \left[f \cdot t - \frac{1}{A} p(t) \right] - \frac{p(t) \cdot V_{sample}}{R \cdot T_{sample}}. \end{aligned} \quad (9)$$

The last term in Eq. (9) is the correction due to the sample volume of the sample which reduces the sample holder volume in Eq. (7). Note that the sample expansion due to hydriding/dehydriding is not taken into account. This is a common inconvenience for mass flow-pcI and Sieverts method—often, volume expansion as a function of hydrogen loading is not known. However, usually, $\Delta V_{sample} \ll V_{dead}$ and therefore this correction is small and can be neglected. The reaction rate is given by

$$\frac{dn_{solid}(t)}{dt} = \frac{p^*}{RT^*} \left[f - \frac{1}{A} \frac{dp(t)}{dt} \right] - \frac{V_{sample}}{R \cdot T_{sample}} \frac{dp(t)}{dt}. \quad (10)$$

The rate depends on the kinetics and inherently on the flow supplied to the material. The main sources of error are dominated by f , which is a characteristic of the MFC, and the pressure measurement. The main sources of error in the measurement are the precision of the flow and pressure measurement. Considering only these two errors using basic error propagation considerations, the error on the amount of hydrogen is given by

$$\Delta n_{solid}(f, p, t) = \frac{dn_{solid}}{df} \Delta f_{error} + \frac{dn_{solid}}{dp} \Delta p_{error}, \quad (11)$$

whereas Δf_{error} and Δp_{error} are the measurement errors of the respective devices. This leads according to Eq. (9) to the expression

$$\begin{aligned} \Delta n_{solid} &= \frac{p^*}{R \cdot T^*} \left(t \cdot \Delta f_{error} - \frac{1}{A} \Delta p_{error} \right) \\ &\quad - \frac{V_{sample}}{R \cdot T_{sample}} \Delta p_{error}. \end{aligned} \quad (12)$$

Therefore, the error on n_{solid} is given by Δf_{error} and Δp_{error} , which are characteristics of the used devices and have to be selected to the best possible standards to improve accuracy, and also a small $1/A$. According to Eq. (8), this translates to a as small as possible apparent system volume; hence the need to construct the apparatus with an as small as possible $V_{connection}$, V_{system} , and V_{holder} and keep those volumes at stable temperatures to achieve best possible accuracy.

By measuring $p(t)$ and using expression (9), the characteristic plot $p(n_{sample})$ can easily be determined. The plateau pressure $p_{plateau}(f)$ is then evaluated by finding the maximum of the density of states (DOS) $D(E)$ of the hydride state.

$$D(E) = \frac{dn}{dE}. \quad (13)$$

The binding energy of hydrogen in equilibrium can be evaluated from the free enthalpy in the gas phase¹⁰ and is given by

$$E = \frac{1}{2} kT \cdot \ln \left(\frac{p}{p_0} \right). \quad (14)$$

According to Eqs. (11) and (12), the $D(E)$ can be reformulated as a function of pressure

FIG. 6. (a) $p(n_{\text{sample}}, T_{\text{sample}}, f)$ for a given, constant flow (b) corresponding DOS of the hydride state. The peak of the DOS corresponds to the plateau pressure $p_{\text{plateau}}(f, T_{\text{sample}})$ for the respective flow f and temperature T .

$$D(\ln p) \propto \frac{dn}{d \ln p}. \quad (15)$$

The DOS of the hydride in an amorphous solid can be described as a Gaussian distribution with the maximum lying at the plateau pressure.^{11–13} Therefore, evaluating $D(p)$ according to Eq. (13) from experimental data will lead to the peak position of the Gaussian distribution and to the corresponding plateau pressure p_{plateau} , as visually depicted in Fig. 6. The procedure mentioned above will lead to p_{plateau} for a given, fixed flow. To determine $p_{\text{equilibrium}} = p_{\text{plateau}}(f=0)$, i.e., the equilibrium state, the same measurement can be performed for different flow rates converging to zero flow. The plateau pressure is then empirically determined by the extrapolation $p_{\text{plateau}}(f \rightarrow 0)$. The so determined values $p_{\text{equilibrium}}$ and T_{sample} can be plotted as a van't Hoff plot to determine the thermodynamic parameters of the material.

The hydrogen adsorption and desorption mechanism is a superposition of different physical mechanisms, comprising H_2 mass transport, dissociative chemisorption, surface migration, transition from chemisorbed to absorbed state (phase transformation), and bulk diffusion.^{14,15} Although analytical models exist for these different aspects, in a real material the contribution of each effect to the final behavior of the plateau pressure is dependent on the material and might even change during the process of adsorption and desorption. While the mathematical models describing each effect differ, they can be linearly approximated near the plateau pressure. In the measurements presented thereafter, a linear extrapolation was chosen for the analysis. Deviations from linear behavior are within the experimental error.

A. LaNi_5 reference measurements

LaNi_5 is probably the most widely characterized metal hydride and therefore serves as a perfectly benchmark for this technique. The sample of $m=359$ mg was fully activated by repetitively evacuating the sample and exposing it to H_2 at a pressure of 30 bars (17 cycles) before the mea-

FIG. 7. Analysis of flow-pcI measurements on LaNi_5 (a) pcI-curves measured at 7 different flow rates at $T_{\text{sample}}=20$ °C. (b) DOS for the measured data. The plateau pressure is evaluated using the maximum of the DOS. The curves were compiled from (a) which are corrected according to Eq. (10) but no smoothing operation or filtering has been applied to the former and each curve consists of 800 (3 SCCM) to 8000 (0.3 SCCM) individual points. While the DOS at 0.3 SCCM shows a Gaussian shape, the measurement at 3 SCCM shows a double peak structure deriving from the kinetic limitation of the material to deliver the required flow.

surements. The BET surface area was measured after the experiments with N_2 and resulted to $0.23 \text{ m}^2/\text{g}$. We present data from desorption measurements because they are not affected by the number of cycles the sample has been subjected to Ref. 1.

Desorption measurements have been performed at $T_{\text{sample}}=20, 30, 40,$ and 50 °C respectively at a minimum of four different flows per temperature in the range $0.3 \text{ SCCM} < f < 3 \text{ SCCM}$ and are shown in Fig. 7. Each curve is collected from one continuous measurement and the data presented is “as-measured” without smoothing. Acquisition was performed every 3 s leading to a point density between 800 ($f=3 \text{ SCCM}$) and 8000 ($f=0.3 \text{ SCCM}$) for each curve and corresponding acquisition time was between 1 and 10 h, respectively. No correction for sample expansion was performed because the correction is well below 0.1% and therefore negligible. For sake of simplicity, only the pcI-curves for $T_{\text{sample}}=20$ °C are shown Fig. 7(a). Similar curve ensembles have been acquired for the other above mentioned isotherms. Two effects are directly observable: The plateau slope decreases with decreasing flow while the plateau pressure increases. Both effects are related to the kinetics of the material with respect to the hydrogen supply rate defined by the flow rate. The quasiequilibrium plateau pressure $p_{\text{plateau}}(f, T_{\text{sample}})$ can be determined according to Sec. II by

FIG. 8. Plateau pressure as a function of flow rate at different temperatures. Full symbols represent measurements at nonzero flow, while the open symbols are extrapolated from these values. Each point is extracted from measurements as depicted in Fig. 7.

calculating the maximum of the DOS. The equilibrium plateau pressure (by definition at zero flow) $p_{\text{plateau}}(f=0, T_{\text{sample}})$ is established empirically by extrapolation of p as a function of flow as represented in Fig. 8. The equilibrium pressure is used to construct the van't Hoff plot to extract the thermodynamic parameters of the sample from the slope and the abscissa according to Eq. (1). For comparison, the data for quasiequilibrium measurements at three flow rates have been plotted along the equilibrium extrapolation in Fig. 9. They show a distinct curvature because the material is not in true equilibrium.

IV. ADVANTAGES OF MASS FLOW-PCI MEASUREMENT

Summarizing the results, the advantages of the mass flow-pcI method are shortly summarized.

- Extrapolation to true equilibrium can be performed by measuring pcI curves at different flow rates and the corresponding quasiequilibrium plateau pressures.
- The flow variation yields information about the kinetics of the material.

FIG. 9. van't Hoff Plot at different flow rates. (The equilibrium state is generated from the extrapolation at flow=0. The measurements at higher flow rate show a slight curvature, showing that the material is not at equilibrium at these flow rates.

- The kinetics of the material can be assessed by the evolution of equilibrium pressure as a function of flow.
- Data acquisition is continuous. The pressure p remains a constant Δp away from equilibrium given by the flow/kinetics of the system.
- Very high point densities lead to extremely precise determination of pcI-curves.
- No intermittent user action is necessary during a measurement (prepare—start measurement—harvest data).
- No valve actuation during the measurement is necessary, leading to strongly reduced wear of components.
- Very low system volume allows for very small samples—a big advantage for measurements where only little sample material is available.

V. SUMMARY

We have presented a new method to determine the thermodynamic parameters ΔH and ΔS of hydrogen storage materials at equilibrium. By this method, true equilibrium data can be obtained by extrapolation to zero flow conditions even when equilibrium is not truly reached. In contrast to the Sieverts method, the mass flow method is operating continuously, increasing the point density on pcI-curves by orders of magnitude while at the same time decreasing the acquisition time dramatically and not relying on the necessity to reach equilibrium. By this method, the accuracy of the determination of thermodynamic parameters could be increased dramatically. The data analysis procedure is depicted in detail by measurements on LaNi_5 as a benchmark material. The equilibrium pressures for the individual isothermal conditions are extracted from measurements at different flows by extrapolation to zero flow. The subsequently extracted values for enthalpy and entropy of desorption from the van't Hoff plot of $\Delta H_d = 32.5 \text{ kJ mol}^{-1} \text{ H}_2$ and $\Delta S_d = 115 \text{ J K}^{-1} \text{ mol}^{-1} \text{ H}_2$ are in perfect agreement with well established literature values.¹⁶

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