Hydrogen sorption studied by manometric (Sievert's) techniques alone and coupled to calorimetry

Introduction

In the Sievert's method, a sample at known pressure and volume is connected to a reservoir of known volume and pressure through an isolation valve. Opening the isolation valve allows new equilibrium to be established. Gas sorption is determined by difference in actual measured pressure (Pf) versus calculated pressure (Pc). The PCTPro is a fully automated Sievert's instrument for the measurement of gas sorption properties of different materials.

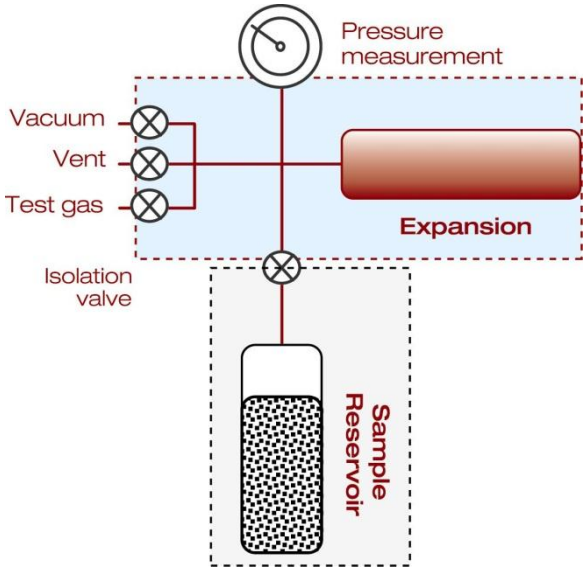

Figure 1 – Principle of Sievert's method

In the PCTPro design, the sample reservoir can be a pressure resistant calorimetric cell, placed in a temperature controlled calorimeter. This way, the heat of sorption can be directly measured. Sensys HPDSC, MicroDSC7, C80 or BT2.15 are typical calorimeters and / or DSC that can be coupled to PCTPro.

1. Hydrogen sorption isotherms on very small samples

With the recent advances in solid state research and the development of new synthesis paths, only small amounts of material are produced. To investigate the sorption properties of these small samples an accurate tool for measurement is required. The microdoser attachment of PCTPro can measure sample quantities down to mg's.

The following data were obtained on a 5.26mg Palladium sample at a temperature of 170°C. Gas injections with DeltaP of 0.3bar in a volume of 0.44mL - i.e. roughly 5 micromoles of H2 - were successively injected in the sample holder. The obtained plateau pressure (2.86 bar) and concentrations (0.621wt% at 5bar) are in line with published data [1].

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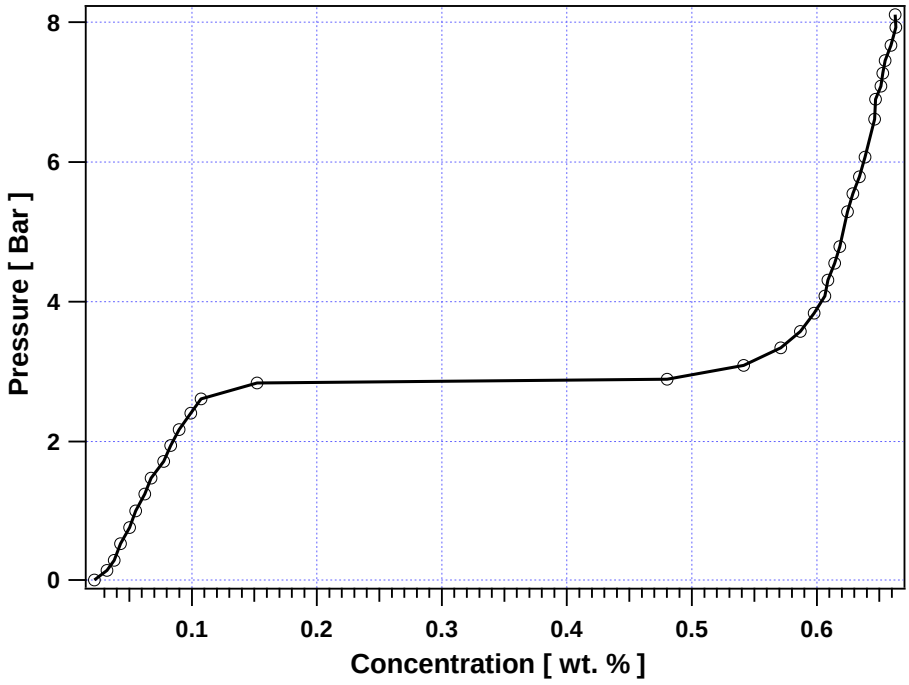

Figure 2 – Hydrogen sorption isotherm at 170°C on a 5.26mg Pd sample

2. Kinetics and thermodynamics of H2 absorption by Palladium at 170°C

The management of the heat released during the formation of a chemical hydride is critical for practical applications. This is particularly true when poorly stable chemical hydrides are involved. It is highly desirable to be able to quantify and validate reaction enthalpies in situ during a sorption measurement. This is made possible with coupled calorimetric and manometric techniques as it is showed in the following example on palladium (Figure 3).

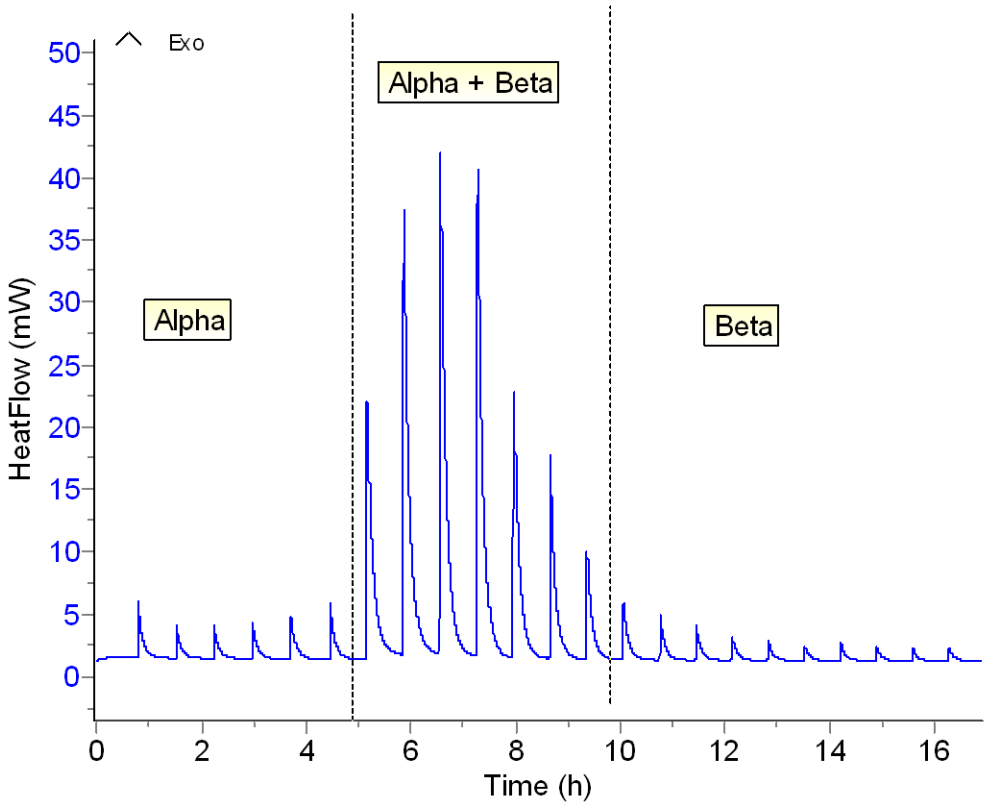

Figure 3 – Heatflow as measured by a C80 calorimeter in PCT mode. The calorimetric cell contained 880mg of Pd and was kept isothermally at 170°C during the whole process. Gas injections with DeltaP of 1bar in a reservoir volume of 5.78mL were programmed.

Each peak corresponds to the injection of one gas dose. The heat evolved increases when the beta phase starts being produced. It corresponds to the plateau observed on the Pd isotherm. The average differential heat of sorption in the alpha phase is found equal to 23.2kJ/mol, which corresponds to the values determined by Lynch et al [2].

Absorption / desorption cycles can also be programmed, leading to results like showed on Figure 4 below. The average heat of absorption is found equal to 35.5kJ/mol, which is comparable to the previous experiment because the integral heat of absorption to reach 7 bar was found equal to 36.4kJ/mol.

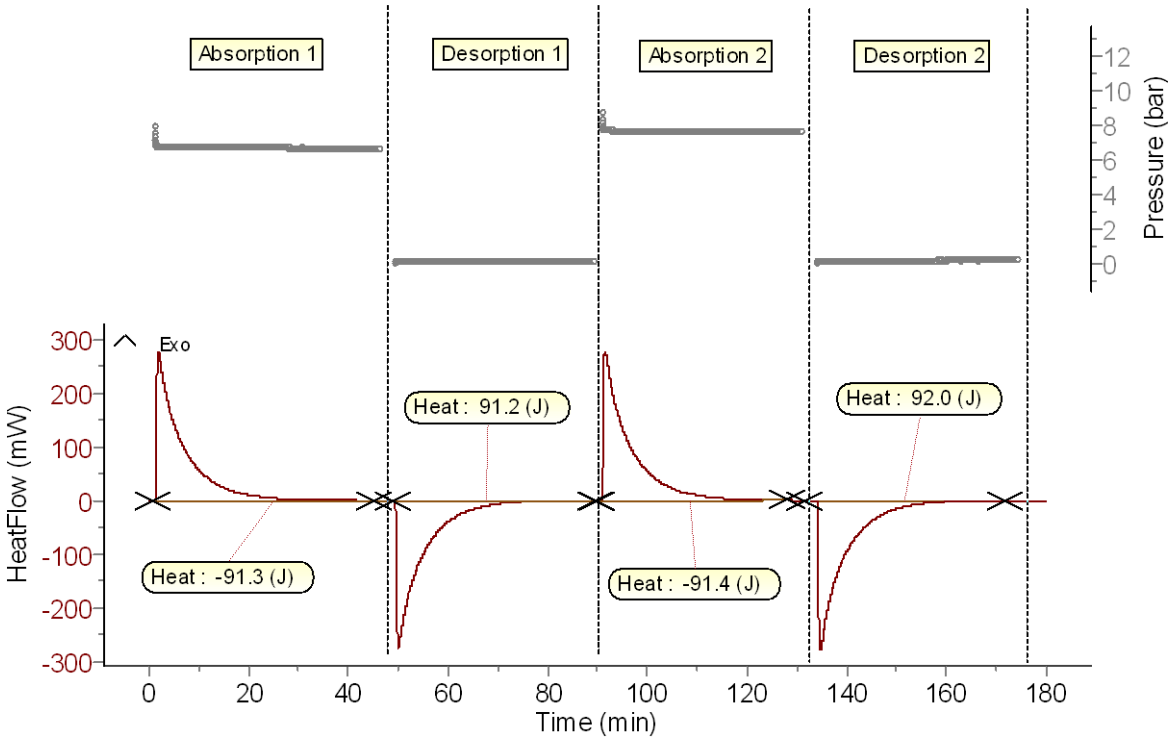

Figure 4 – Heatflow as measured by a C80 calorimeter in kinetics mode. Two adsorption / desorption cycles were programmed between 7 bar and 0.15 bar.

3. Hydrogen adsorption on MOF-5 at 87K monitored by simultaneous manometric-calorimetric techniques

Metal-organic frameworks (MOFs) are interesting porous materials because their properties can be tailored for specific applications. Today these structures are envisaged for multiple applications in gas adsorption, like hydrogen storage, selective adsorption of CO2 against CH4, or CO2 against H2. The MOF-5 (fig 2.) is chosen as an example of a commercially available Metal Organic Framework to demonstrate the capacities of coupled Sievert's technique and heat flow calorimetry at very low temperature.

The hydrogen sorption isotherm of a 180mg sample of MOF-5 at 87K was obtained thanks to a PCTPro-BT2.15 coupled experiment. The obtained capacity values are similar to published data [3].

This low temperature calorimeter allowed measuring the heat evolved during the successive hydrogen injections. The differential heat of adsorption data are also calculated. The integral heat of adsorption is found equal to -4.19kJ/mol, which is comparable to literature values [4].

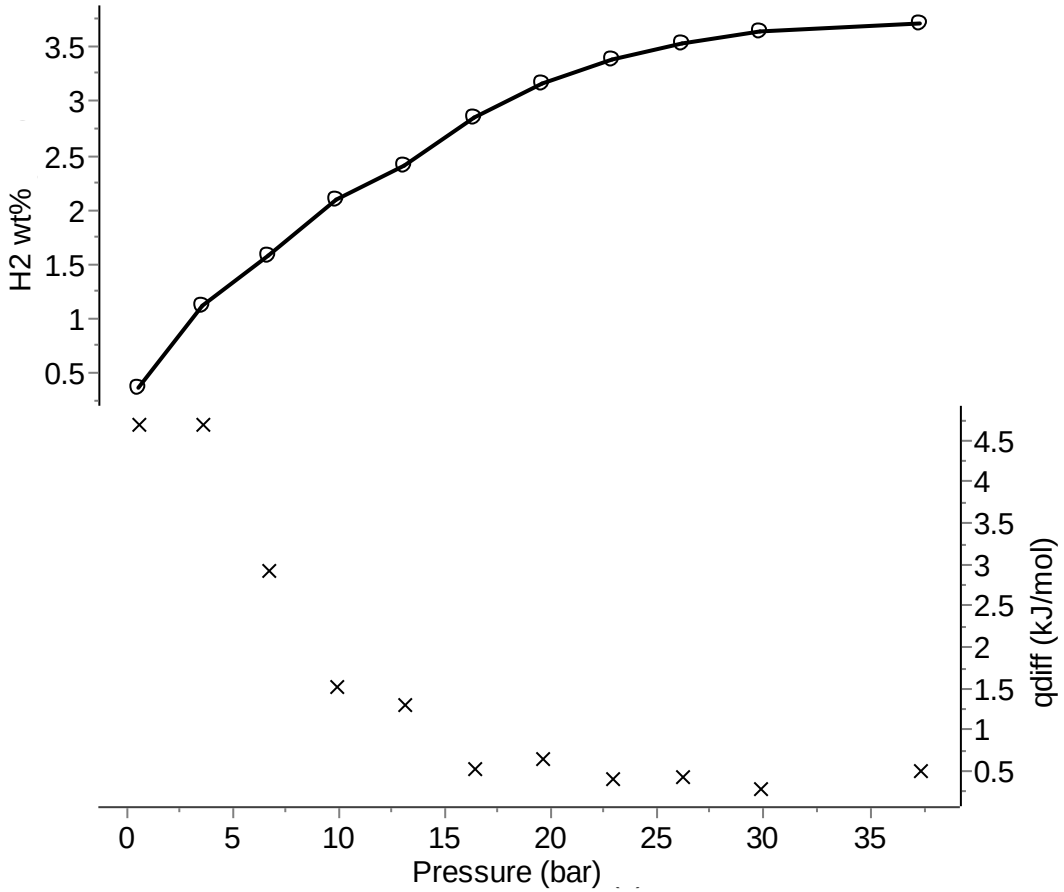

Figure 5 – H2 adsorption isotherm on MOF-5 at 87K and differential heat of adsorption as measured simultaneously by the BT2.15 calorimeter

[1] Wicke, E., Brodowsky, H., In Hydrogen in Metals I, Alefeld, G., Völkl, J., Eds., Springer: Berlin, Vol. 1 (1978), 73

[2] J. F. Lynch and Ted B. Flanagan , J. Chem. Soc., Faraday Trans. 1, 1974,70, 814-824

[3] M. Hirscher et al, Microporous and Mesoporous Materials 129 (2010) 335–339

[4] B. Schmitz et al, ChemPhysChem, Volume 9, Issue 15, pages 2181–2184 (2008)

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