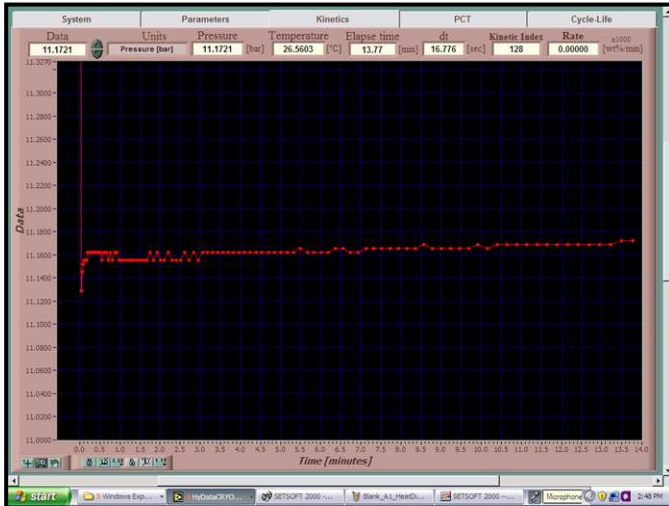
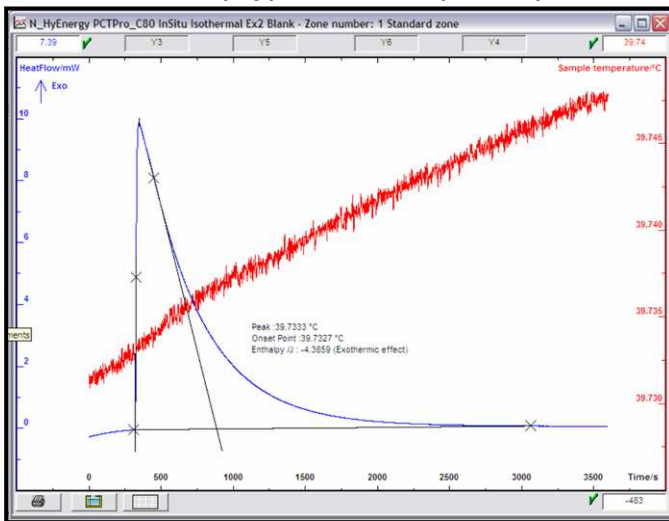


**Combined calorimetry and hydrogen sorption measurements on LaNi<sub>5</sub>**

**Introduction:** The thermodynamic stability of hydrides is a key parameter for practical applications in hydrogen storage. The measurement of the enthalpy of reaction in-situ during the gas sorption is particularly useful for unstable chemical hydrides where the H<sub>2</sub> sorption is not reversible under normal conditions . By coupling a C80 and a PCTPro 2000, we can simultaneously quantify the heat of formation of the hydride and its hydrogen sorption capacity.



Effect of gas heating at 11.2 bar PCTPro 2000 (top) and on C80 (bottom)



**Experimental**

The adsorption and desorption of H<sub>2</sub> by a LaNi<sub>5</sub> alloy was studied using a PCTPro- 2000 coupled with a C80.

Initially, a background was recorded without sample.

Then the powder (5 g) was analyzed using the following procedure:

- Activation of the powder by H<sub>2</sub> absorption/ desorption cycles at 40 °C.
- Measurement of the heat of reaction on the 20th cycle at 40 °C.

**Background measurement**

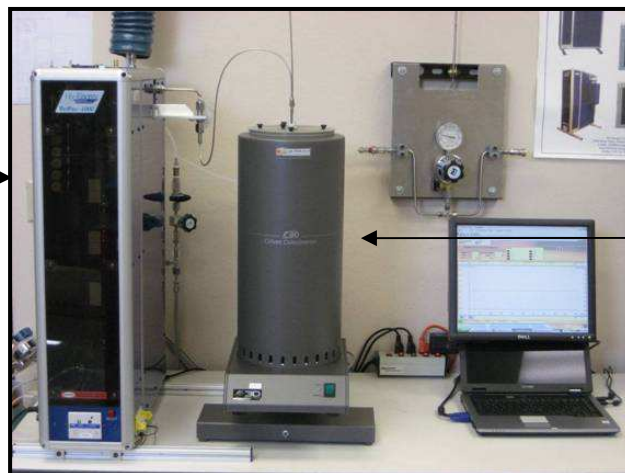
The C80 signal obtained without sample not only showed that the influence of the heating on the gas is negligible but, in addition, the measurement provided an accurate measurement of the heat capacity C<sub>p</sub> of hydrogen gas.

Measured effect of gas heating 6 ml at 11.2 bar:

- → 29.8 J/K mol H<sub>2</sub> ~ C<sub>p</sub>,
- Baseline heating of gas ~ 0.3 kJ/mol H<sub>2</sub> equivalent to a 1% effect on the measurement of the heat of hydride formation.

**Instrument**

PCTPro-2000  
Gas sorption  
Sievert's apparatus  
-260 to 500°C

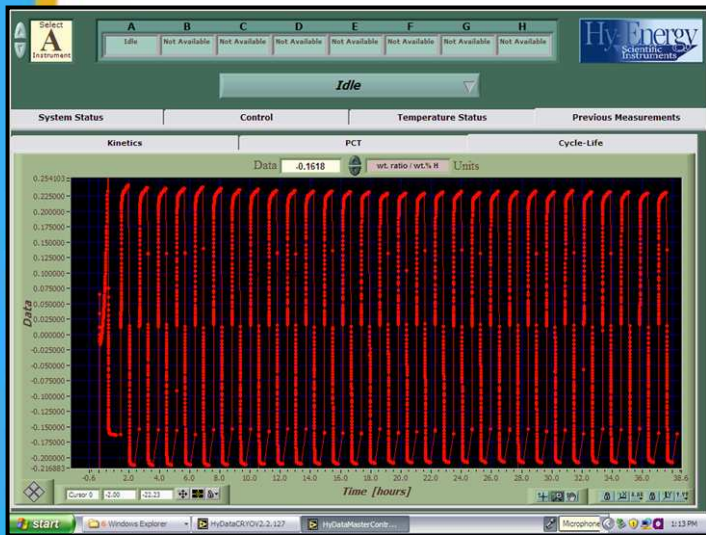


**Instrument**

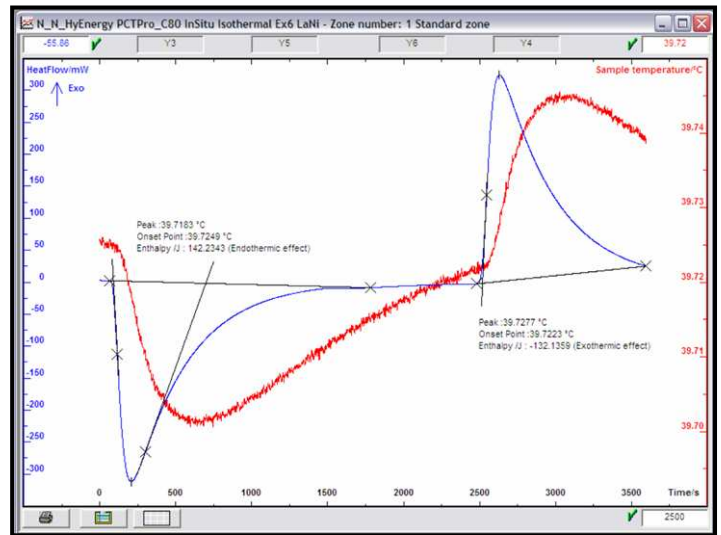
C80  
Calorimeter  
Ambient up to 300°C

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Activation Absorption (11 bar) and Desorption (vacuum) cycles at 40 °C



Calorimetry on cycle 20

## Results

The analysis of the results demonstrates that:

- 1) Hydriding was steady but incomplete after more than 30 cycles. The material only reached 1/6 the full theoretical capacity.
- 2) This behavior is verified by the morphology of the powder following the sorption tests. Only 1/6 of the sample powder (fine grains) were hydrided.



Sample after 32 cycles

- 3) Using the hydrogen sorption capacity measured by the PCTPro-2000, the heat of reaction measured using the C80 was in accordance with the theoretical heat of formation of the hydride.<sup>1</sup>

- 4.377 gm  $\text{LaNi}_5 \leftrightarrow 1/6 \text{ LaNi}_5\text{H}_6$ .
- Measured: 0.004875 moles  $\text{H}_2$ .
- $\Delta H$ : 142.2 J = 29.2 kJ/mol  $\text{H}_2$ .

## Conclusion

This example demonstrates the importance of measuring simultaneously the quantitative hydrogen uptake and release to obtain the true enthalpy of reaction. This is particularly true for unstable chemical hydrides where the  $\text{H}_2$  sorption is not reversible under normal conditions preventing enthalpy determination from equilibrium pressure measurements.

***The coupling of the PCTPro-2000 and C80 instruments provides a powerful new tool for accessing the thermodynamics of gas/solid reactions.***

1. Zhang, D. X. , X. L. Wang, and G. S. Wang ,“Recovery of Efficacy-Lost  $\text{LaNi}_5$  by Chemical Preparation Method”, Zeit. Phys. Chem. NF, 164, 1989, pg 1441