Best Practices for Characterizing Hydrogen Storage Properties of Materials

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ST052

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Overview

Timeline

- Start – Feb 2007
- End – Sept 2010
- 90% complete

Budget

- Total project funding
  - DOE $892K
  - Contractor $178K
- Funding FY09 $270K
- Funding FY10 $222K

Barriers

- Technical Targets: On-Board Hydrogen Storage Systems
- Barriers addressed
  - A. System Weight and Volume.
  - C. Efficiency.
  - D. Durability/Operability.
  - E. Charging/Discharging Rates.
  - J. Thermal Management.
  - Q. Reproducibility of Performance.

Partners

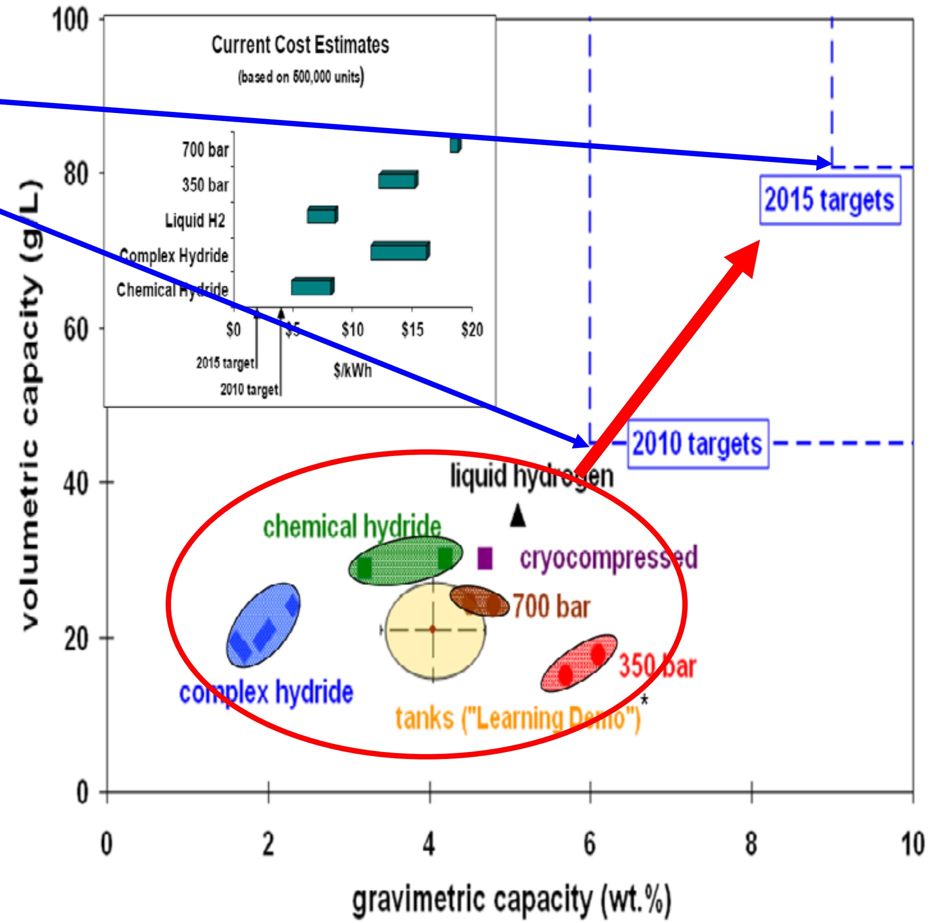
- NREL: Dr. Parilla, Contract Management
- Authors: University of California Berkeley- California Institute of Technology - Pacific Northwest Laboratories - Texas A&M University - Los Alamos National Laboratory - Université Paris-Sud - VU University Amsterdam and the Delft University of Technology - University of Nevada Reno
- IEA Task 22, Dr. Kuriyama AIST, Japan
- Review by experts: IEA Task 22 & others

Relevance

- The EERE and Fossil Energy are working to develop innovative materials for reversible hydrogen storage including high surface area adsorbents, metal organic frameworks, and metal hydrides, as well as approaches that are regenerable off-board such as chemical hydrides and liquid carriers.
- There are many challenges in the accurate characterization of the hydrogen storage properties of new materials.
- There is a need for consistent measurement practices and improved communication of technical results.
- This project addresses this need through the creation of a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials.
- The initial sections of this document have been made available for public use by pdf download from the DOE website.
- The project is on schedule for the remaining 2 sections.

Relevance to Program Targets

Table 3.3.2 Technical Targets: On-Board Hydrogen Storage Systems				
Storage Parameter	**Units**	**2007**	**2010**	**2015**
System Gravimetric Capacity				
Usable, specific-energy from H_2	kWh/kg	1.5	2	3
(net useful energy / max system mass) [a]	(kg H_2/kg system)	(0.045)	(0.06)	(0.09)
System Volumetric Capacity				
Usable energy density from H_2	kWh/L	1.2	1.5	2.7
(net useful energy / max system volume)	(kg H_2/L system)	(0.036)	(0.045)	(0.081)
Storage System Cost [b] Fuel cost [c]	\$/kWh net (\$/kg H_2) \$/gge at pump	6 (200) ---	4 (133) 2-3	2 (67) 2-3
Durability / Operability				
Operating ambient temperature [d]	ºC	-20/50 (sun)	-30/50 (sun)	-40/60 (sun)
Min/max delivery temperature	ºC	-30/85	-40/85	-40/85
Cycle life (1/4 tank to full) [e]	Cycles	500	1000	1500
Cycle life variation [f]	% of mean (min) at % confidence	N/A	90/90	99/90
Min delivery pressure from tank; FC = fuel cell, ICE = internal combustion engine	Atm (abs)	8FC / 10 ICE	4FC / 35 ICE	3FC / 35 ICE
Max delivery pressure from tank [g]	Atm (abs)	100	100	100
Charging / Discharging Rates				
System fill time (for 5 kg)	min	10	3	2.5
Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
Start time to full flow (20 ºC) [h]	s	15	5	5
Start time to full flow (- 20 ºC) [h]	s	30	15	15
Transient response 10%-90% and 90% - 0% [i]	s	1.75	0.75	0.75
Fuel Purity (H_2 from storage) [j]	% H_2	99.99 (dry basis) See Appendix C		
Environmental Health & Safety				
Permeation and leakage [k]	Scc/h	Meets or exceeds applicable standards		
Toxicity	-			
Safety	-			
Loss of useable H_2 [L]	(g/h)/kg H_2 stored	1	0.1	0.05



Accurate measurement methods and metrics are required to determine how new materials compare to all of these targets.

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Objectives

What ?

- ***To prepare a reference document detailing best practices and limitations in measuring hydrogen storage properties of materials***
- Document reviewed by experts in the field (IEA, IPHE, Industry)
- Document to be made available to researchers at all levels in the DOE hydrogen storage program

Why ?

- To reduce errors in measurements
- Improve reporting and publication of results
- To improve efficiency in measurements
- Reduce the expenditure of efforts based on incorrect results
- Reduce the need for extensive validation
- To increase the number of US experts in this field (students, etc.)

Benefit to DOE and Researchers

- The transfer the knowledge and experience in making critical performance measurements from experts in this field to the entire DOE hydrogen storage research community.
- Provide a published resource to aid those just entering to this rapidly expanding field.
- Aid in the establishment of uniform measurement practices and presentation of performance data.
- Improve international communications on these issues between government, university, small and large business entities.

Milestones - 2009/2010

Milestone	Results	%Comp
Finalize Kinetics section	Kinetics section reviewed by many experts all contribution integrated into final version.	100%
Finalize Introduction	Preface and Introduction section completed. Sections reviewed and finalized.	100%
Prepare draft Capacity Section	Draft completed with contributions from UC Berkeley, Caltech and PNNL	100%
Finalize Capacity Section	Draft reviewed and presented online for public comment which was integrated into final version	100%
Finalize Thermodynamic section	Final contributions of the Thermodynamic section are underway and the process of review will begin shortly.	80%
Draft Cycle-Life Section	Draft version of the Cycle-life section in progress.	50%

- **Go/No-Go FY10:** Project slated to end (9/2010).

Approach - Overview

- **Task 1: General Introduction** * (Added at request of DOE)
  - General introduction to hydrogen storage materials R&D.
  - Overview of measurement techniques and best choice related to purpose of study.
  - Overview of common errors and accuracy of these techniques.
- **Task 2: Kinetics**
  - Emphasis on measurement conditions and material properties that strongly influence the results of kinetic measurements
  - Benefits and limitations of applying mechanistic analysis to kinetics data.
- **Task 3: Capacity**
  - Hydrogen capacity has been the key metric for the success and failure of materials to be considered for practical hydrogen storage.
  - The objective of this task is to clarify issues that can impact these measurements.
- **Task 4: Thermodynamic Stability**
  - Review methods for precisely determining equilibrium thermodynamics.
  - Define protocols to separate true equilibrium conditions from kinetic effects.
  - Present new measurement techniques for the rapid thermodynamic analysis.
- **Task 5: Cycle-life Properties**
  - Cycle-life measurements are critical for evaluating the performance of hydrogen storage materials for applications where hundreds of cycles will be required.
  - Define how such tests should be performed, what parameters may impact the results, and what properties are e.g., capacity fade, or degradation in kinetics, are most critical in performance evaluation.

Key Accomplishments

- *Task 1: Final Introduction section 100% complete.*
- *Task 2: Final Kinetics section 100% complete.*
- *Task 3: Capacity section in progress 100% complete.*
- *Task 4: Draft version Thermodynamic section 80% complete.*
- *Task 5: Draft version Cycle Life section in progress 50% complete.*
- *Participation as project in IEA Task 22.*
- *Contributions and editorial reviews by many world experts.*
- *Reviewed Tasks 1-3 Document Delivered to DOE Dec. 2009.*
- *Public comment received and integrated into document.*
- *Final Tasks 1-3 Document Posted to DOE website for world-wide access.*

Please download the current Best Practices document from:

http://www1.eere.energy.gov/hydrogenandfuelcells/storage/test_analysis.html

Collaborations

- **Contributions to this project from world experts including written materials, examples, presentation or editorial review of draft documents from:**
  - Dr. Philip Parilla and Dr. Thomas Gennett, National Renewable Energy Laboratory, Golden CO, USA.
  - Dr. Gary Sandrock of the U.S. Department of Energy.
  - Dr. George Thomas of the U.S. Department of Energy.
  - Professor Sam Mao University of California Berkeley.
  - Dr. Michael Miller of Southwest Research Institute®, San Antonio TX.
  - Dr. Anne Dailly, and Dr. Frederick Pinkerton of General Motors GM R&D Center.
  - Professor Channing Ahn, California Institute of Technology, USA, IEA Task 22.
  - Professor Richard Chahine, Université du Québec à Trois-Rivières, Canada, IEA Task 22.
  - Professor Evan Gray, Griffith University, Brisbane, Australia , IEA Task 22.
  - Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller Norway.
  - Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi , AIST, Japan, IEA Task 22.
  - Dr. Eric Poirier of NRC Canadian Neutron Beam Centre Chalk River Laboratories, Canada
  - Dr. Kevin Ott, Dr. Anthony Burrell, and Dr. Troy Semelsberger of Los Alamos National Laboratory
  - Professor Klaus Yvon, University of Geneva, Switzerland

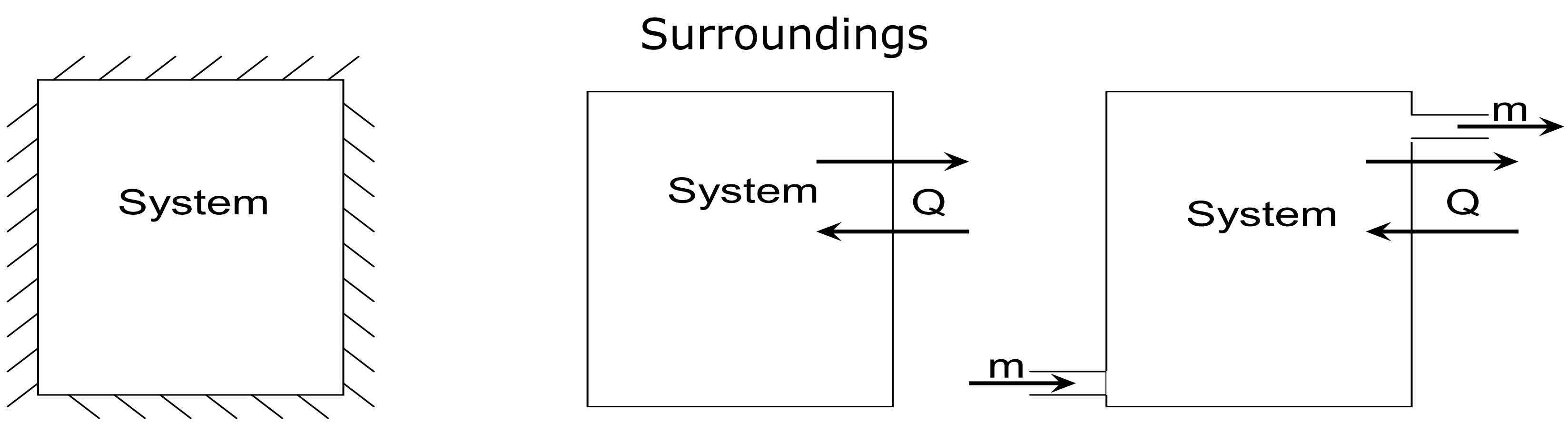
Response to 2008 Reviewers Comments

- ***Relevance:*** "This project will be a huge benefit tot the field". Our objective is to aid the key issue of measurement methods and accuracy that are most relevant to the program and to disseminate this to a world-wide audience.
- ***Approach:*** "Presently the approach comprises individual tasks that address topics on kinetics, capacity, thermodynamics, and cycle-life. A task devoted to instrumentation for each of the measurement techniques and other laboratory requirements, such as gas-source purity, should be included as a separate chapter of the final document". We have added more detail on these topics in the introduction with a section on measurement techniques, as well as laboratory requirements and the impact of such issues as gas source purity on measurements (this is covered throughout the document, in particular in the Capacity measurement section). "Considering that materials preparation plays such a key role in hydrogen storage experiments, there may be some logic in including a section focusing on (at least) ball milling and "activation" techniques." The subject of materials preparation has been addressed in more detail in the Capacity measurement section of the document.
- ***Accomplishments:*** "The project's technical accomplishments are progressing on schedule".
- ***Technology Transfer / Collaborations:*** "It is nice to see many different experts involved in the effort". IEA task 22 is providing a great venue to present information and to establish the participation of experts in this project. We have also setup an open web-based system to receive input from the entire international community.
- ***Future Work:*** "There is no information on borohydrides, a group of materials currently of great interest for high-capacity, light weight applications. These materials are fairly reversible, and thus challenging, for performing reproducible and accurate measurements. " " Add a chapter on borohydrides, and also expand the discussion of amide materials". This is being included to a limited extent in the Cycle-Life chapter. Given the opportunity, a separate chapter on the subject will be considered.

Section 4: Thermodynamics

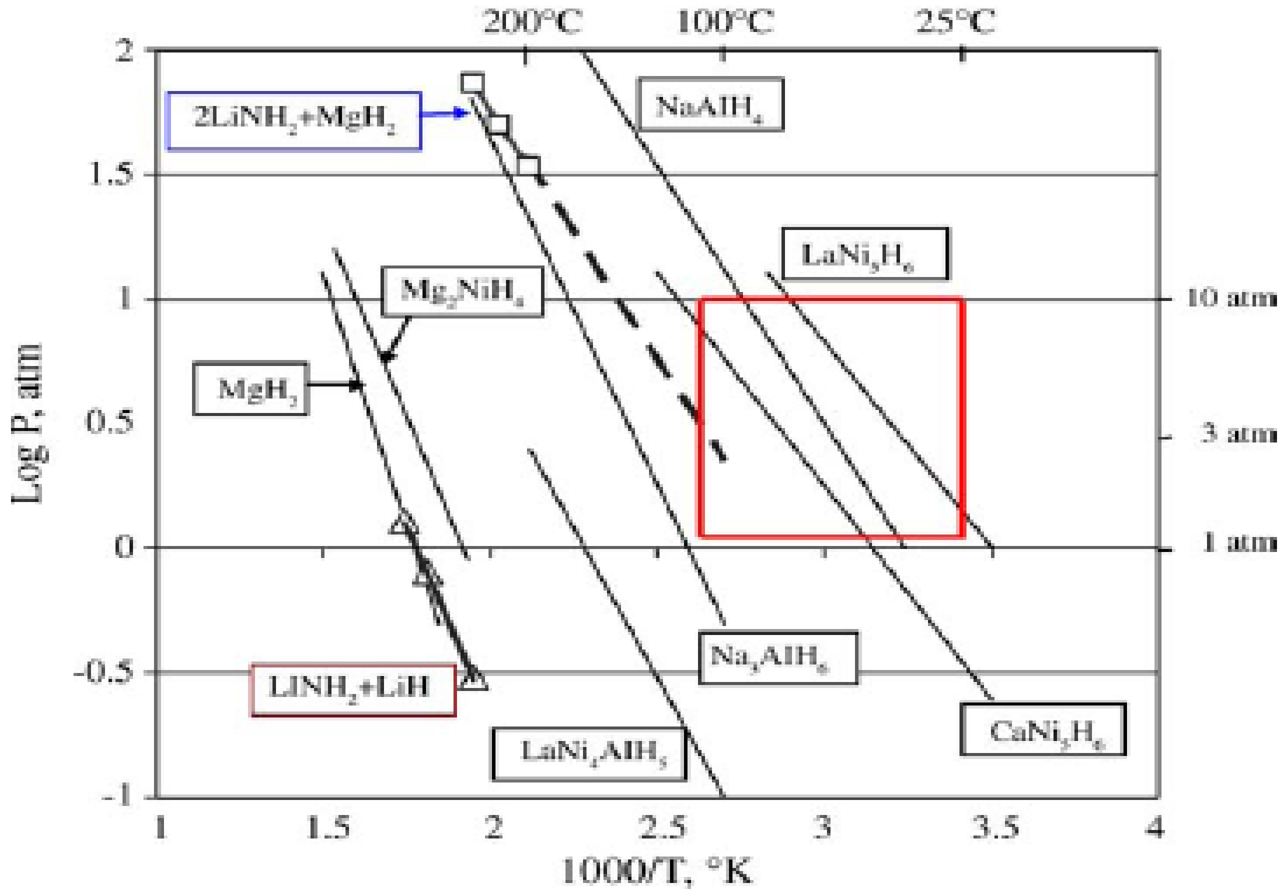
Examples: Task 4 Thermodynamics

Introduction/Definitions: The definition of the system under consideration is fundamental to the study of thermodynamics. A thermodynamic system is separated from its surroundings, often called the environment, by an arbitrarily defined boundary. The properties of the boundary, such as whether it is fixed or flexible, or allows the exchange of quantities such as mass or energy, determine the type of system. The state of each type of system can be completely determined by the measurement of a set of independent variables. In most cases, only three state variables are required, but by taking advantage of constant properties defined in a given system, this requirement can usually be reduced to only two.



Diagrams of a) isolated system, no exchange with surroundings,
b) closed system, only exchanges heat with surroundings, and
c) open system exchanging both heat and mass with surroundings

Thermodynamic Stability - Reversible Hydride Materials



Van't Hoff plot of equilibrium pressure vs. temperature. Boxed area represents practical P and T for PEM fuel cell applications. Note: thermodynamic equilibrium is independent of time. The kinetics of hydrogen absorption and desorption are very different for the materials shown and may limit the practical ability to operate within the boxed area for many materials.

Typical Thermodynamic Measurements: Volumetric PCT - Reversible Hydride Materials

Van't Hoff relationship between equilibrium pressures and temperatures provide the enthalpy and entropy of hydride formation

$$\ln\left(\frac{P_{eq}}{P_o}\right) = \frac{\Delta H_f^o}{RT} - \frac{\Delta S_f^o}{R}$$

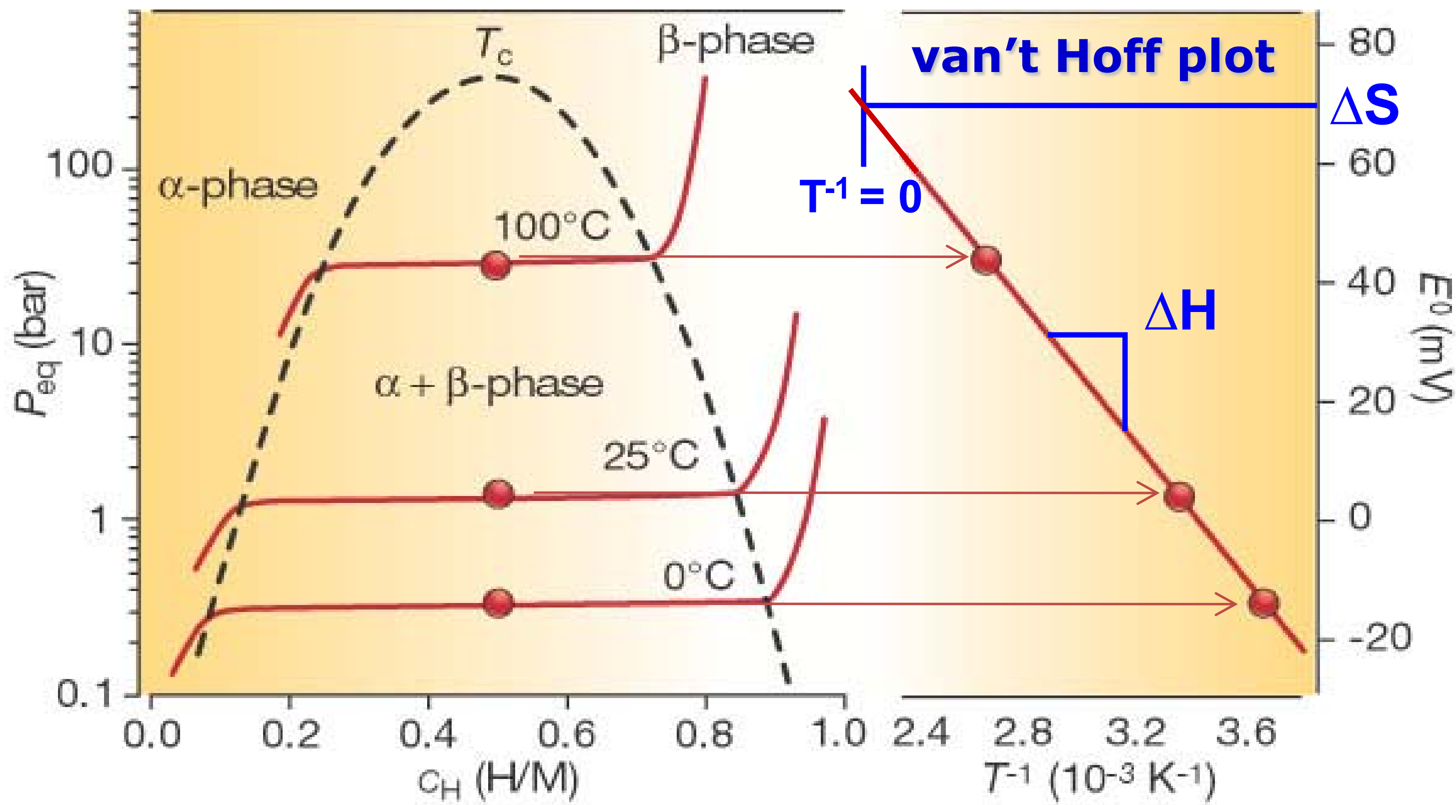
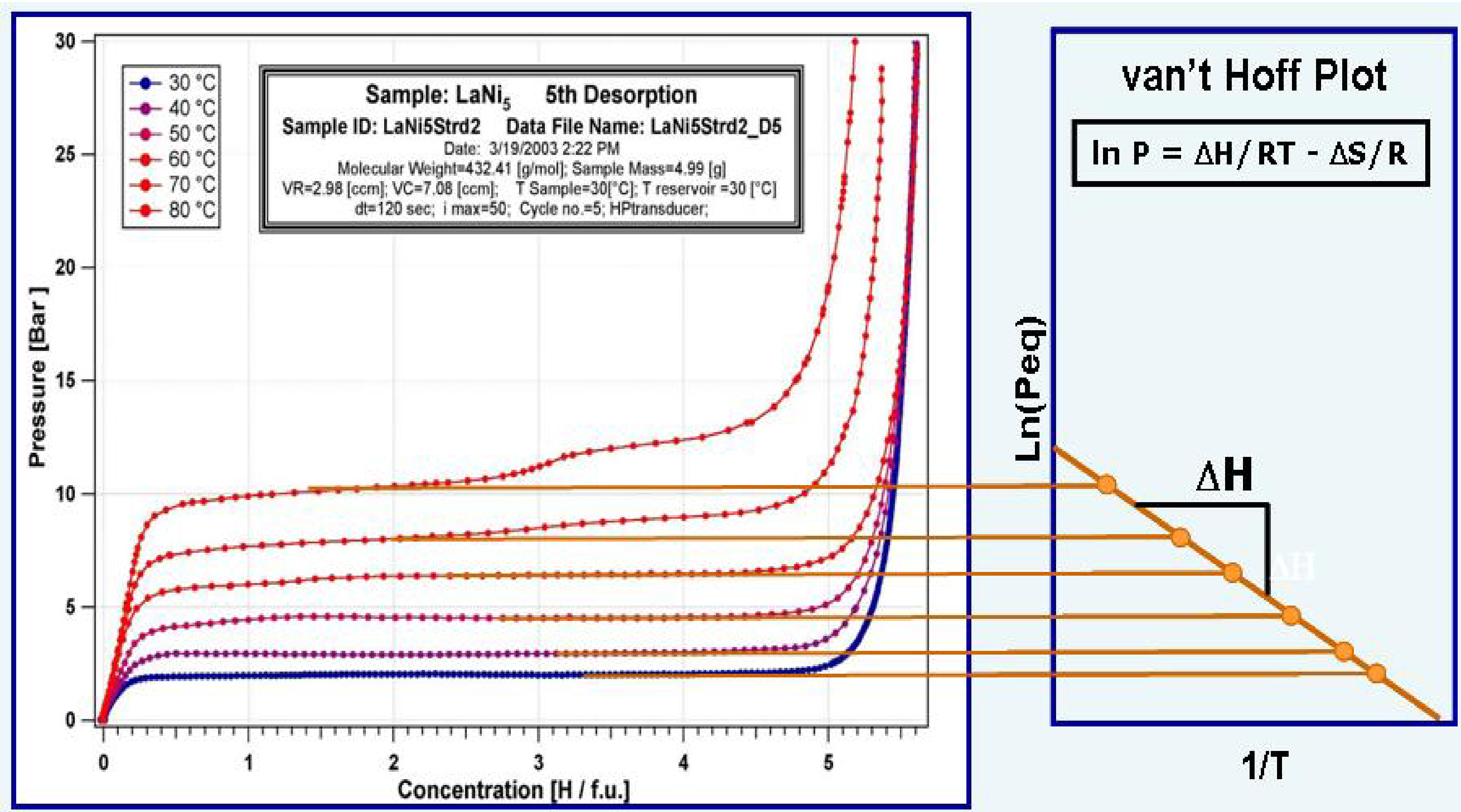


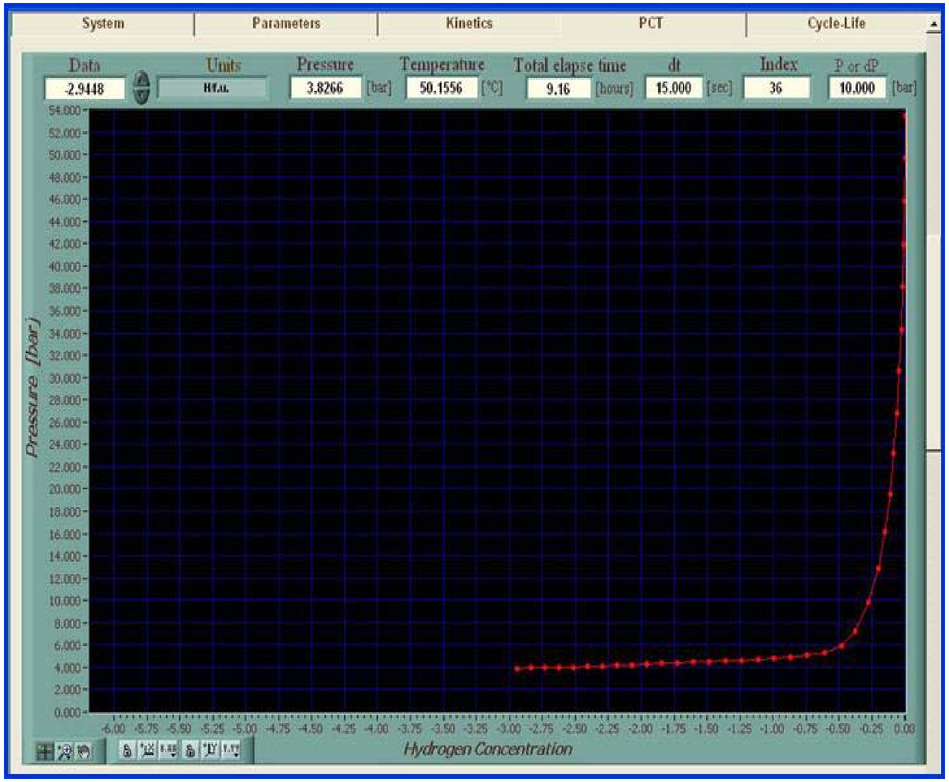
Illustration of the construction of a van't Hoff plot from a series of PCT measurements at different temperatures.

Example: Volumetric PCT Measurements Reversible Hydride Materials



Standard method of making a van't Hoff plot from a series of desorption PCT measurements at different temperatures $LaNi_5$.

Example: "Direct van't Hoff" PCT Measurements Reversible Hydride Materials



Desorption PCT measurement on $LaNi_5$ at 50°C. Dosing is stopped at a specific hydrogen concentration (3 H/f.u.).

Pressure/time profile: the sample is reduced to room temperature then increased in steps of 10°C. Equilibrium pressures are measured at each temperature step.

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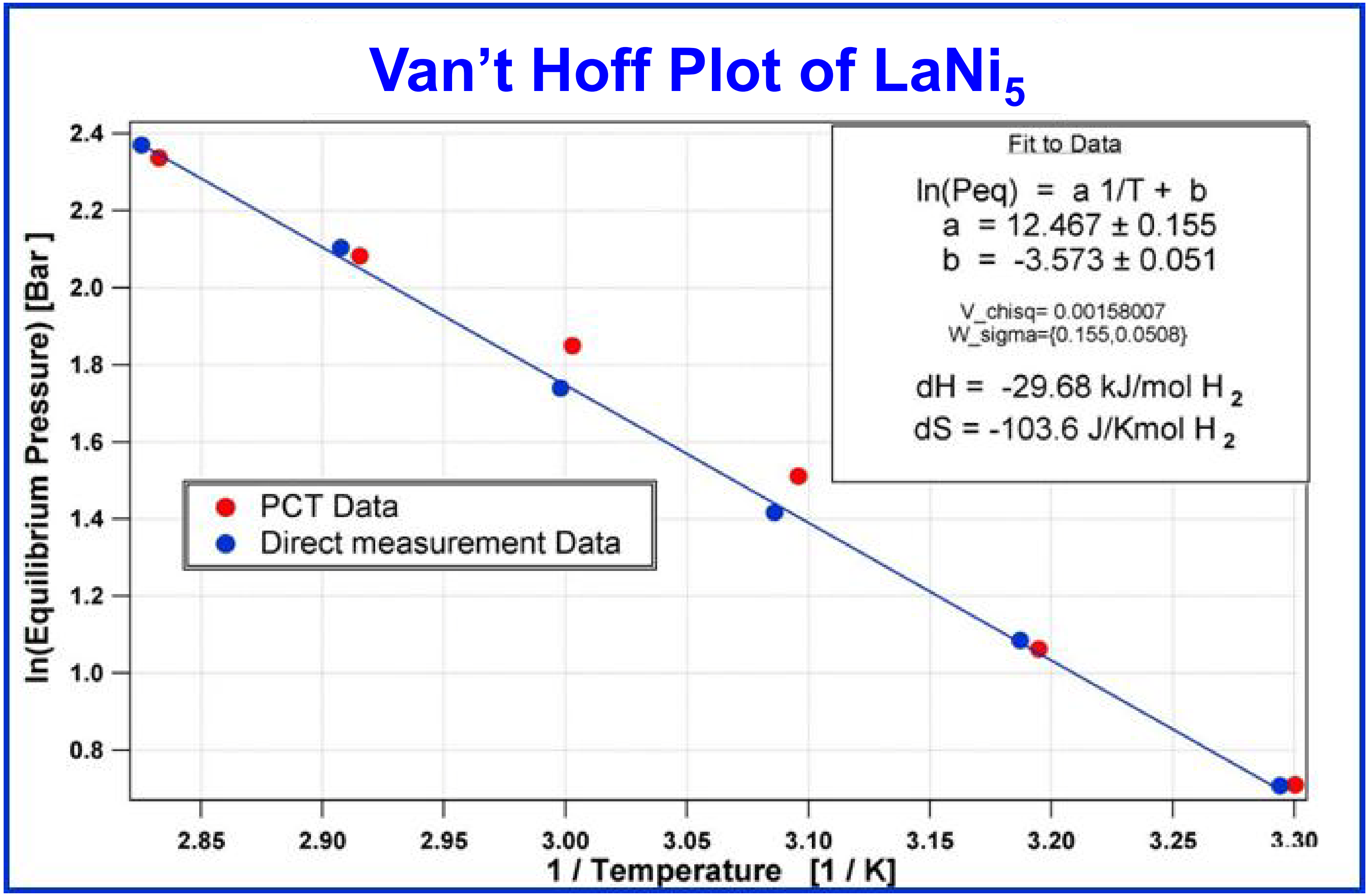
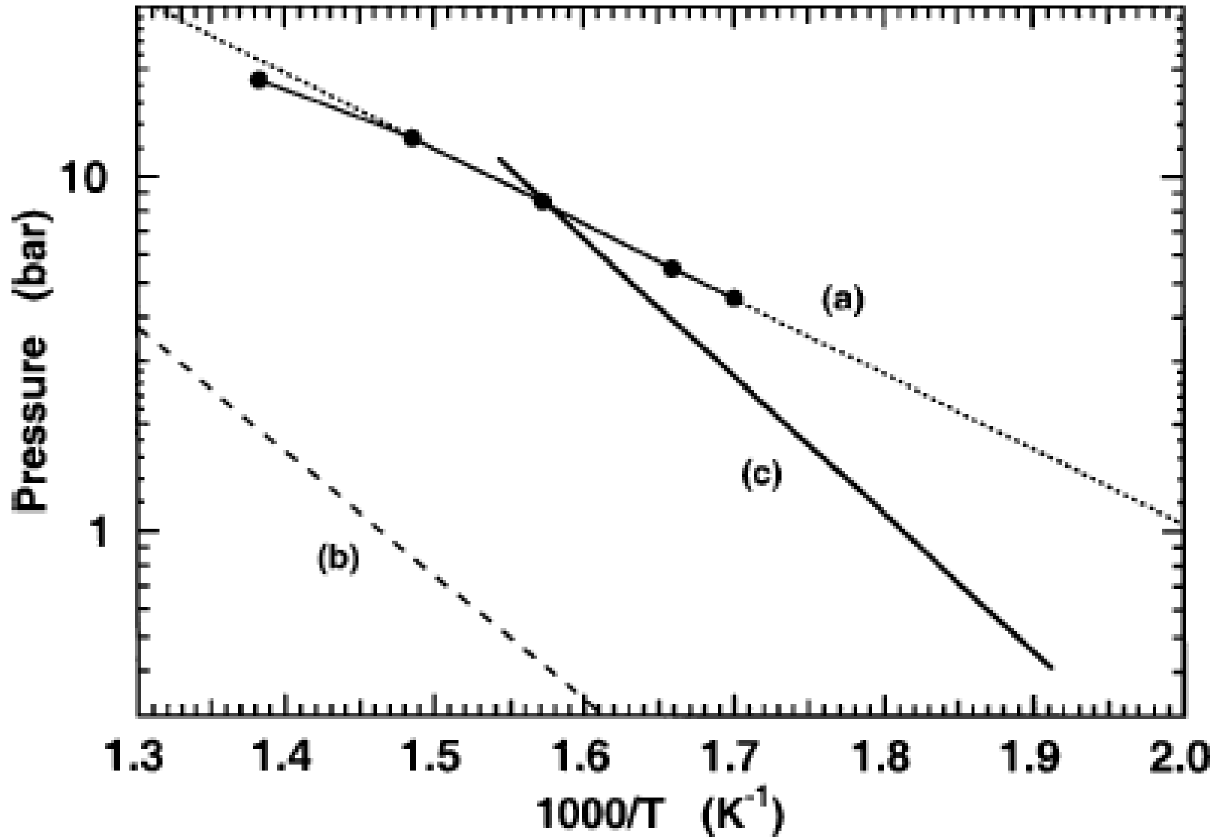
Example: PCT vs. "Direct van't Hoff" Volumetric Measurements - Reversible Hydride Materials



Van't Hoff plot from a series of PCT measurements (red) and a single "Direct van't Hoff" measurement on LaNi5 from 30°C to 80°C.

Example: Destabilization of Hydride Materials



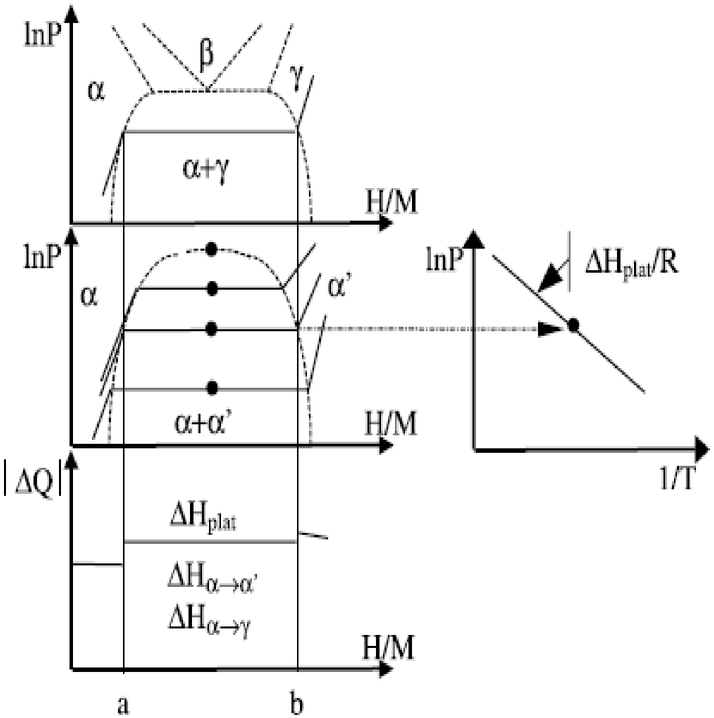
Van't Hoff plots of (a) $LiBH_4$ destabilized with MgH_2, (b) pure $LiBH_4$ and (c) pure MgH_2. The points on curve (a) are the measured data, the curve is extended to show a temperature of 225°C at an equilibrium pressure of 1 atm. Slow kinetics require measurements at high temperature and extrapolation of thermodynamics to lower temperatures.

J.J. Vajo, S.L. Skeith, F. Mertens, „Reversible Storage of Hydrogen in Destabilized LiBH4" J. Phys Chem. B 109 (2005) 3719-3722

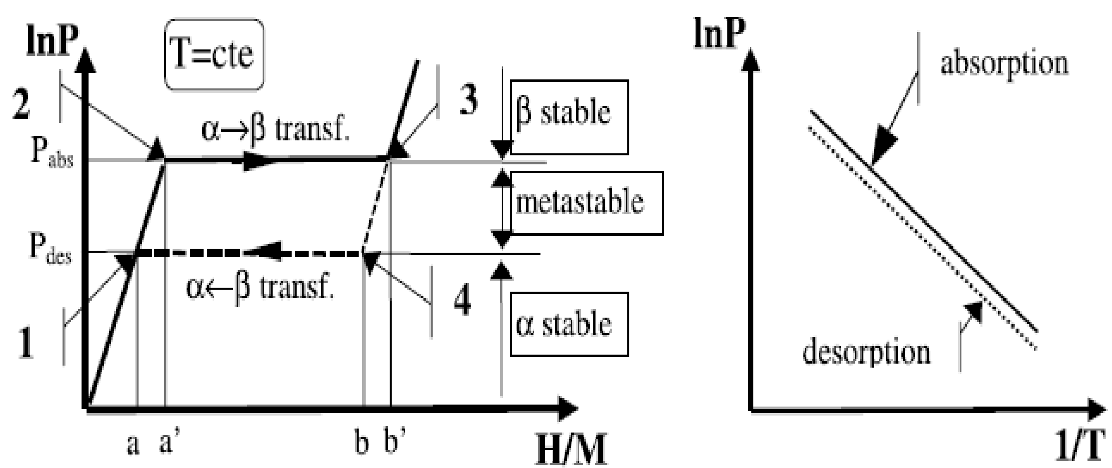
Consideration: Hysteresis -Reversible Hydrides

(a)

Intrinsic hysteresis is observed for nearly all metal hydrides.



(b)



(a) Isotherms for a structural transformation system (top) and a miscibility gap system (middle). Heat evolved during H absorption (bottom). Van't Hoff plot derived from the plateau pressures (right). (b) Isothermal hysteresis (left), reversible paths: 1–2 & 3–4; irreversible: 2–3 & 4–1; effect of hysteresis on van't Hoff plot (right).

P. Dantzer, "Properties of intermetallic compounds suitable for hydrogen storage applications" Mat. Sci and Eng. A329-331 (2002) 313-320

Theory: Hysteresis - Reversible Hydrides

Potential reasons for intrinsic hysteresis in metal hydrides.

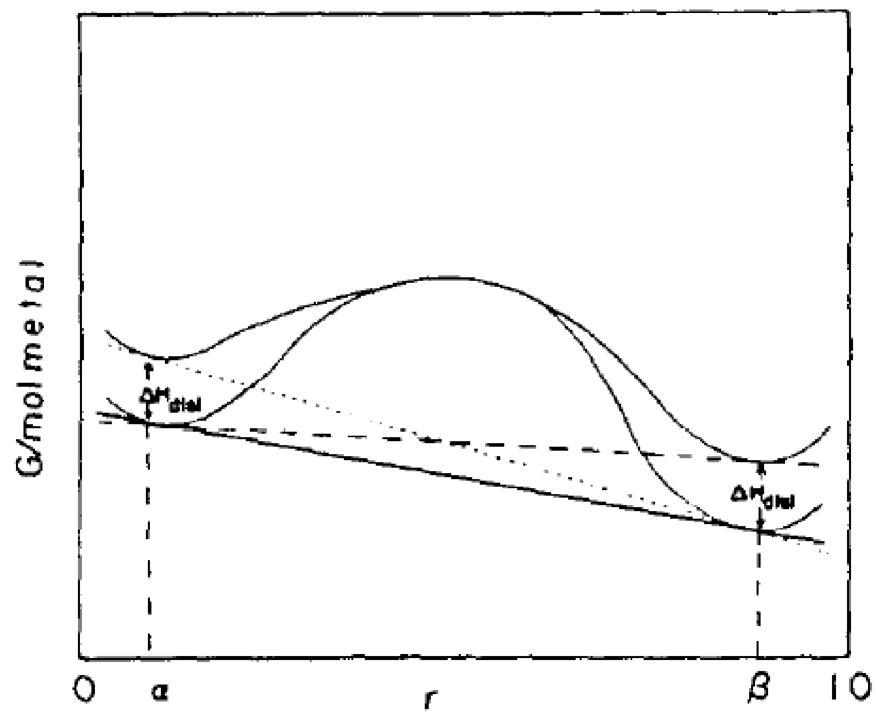
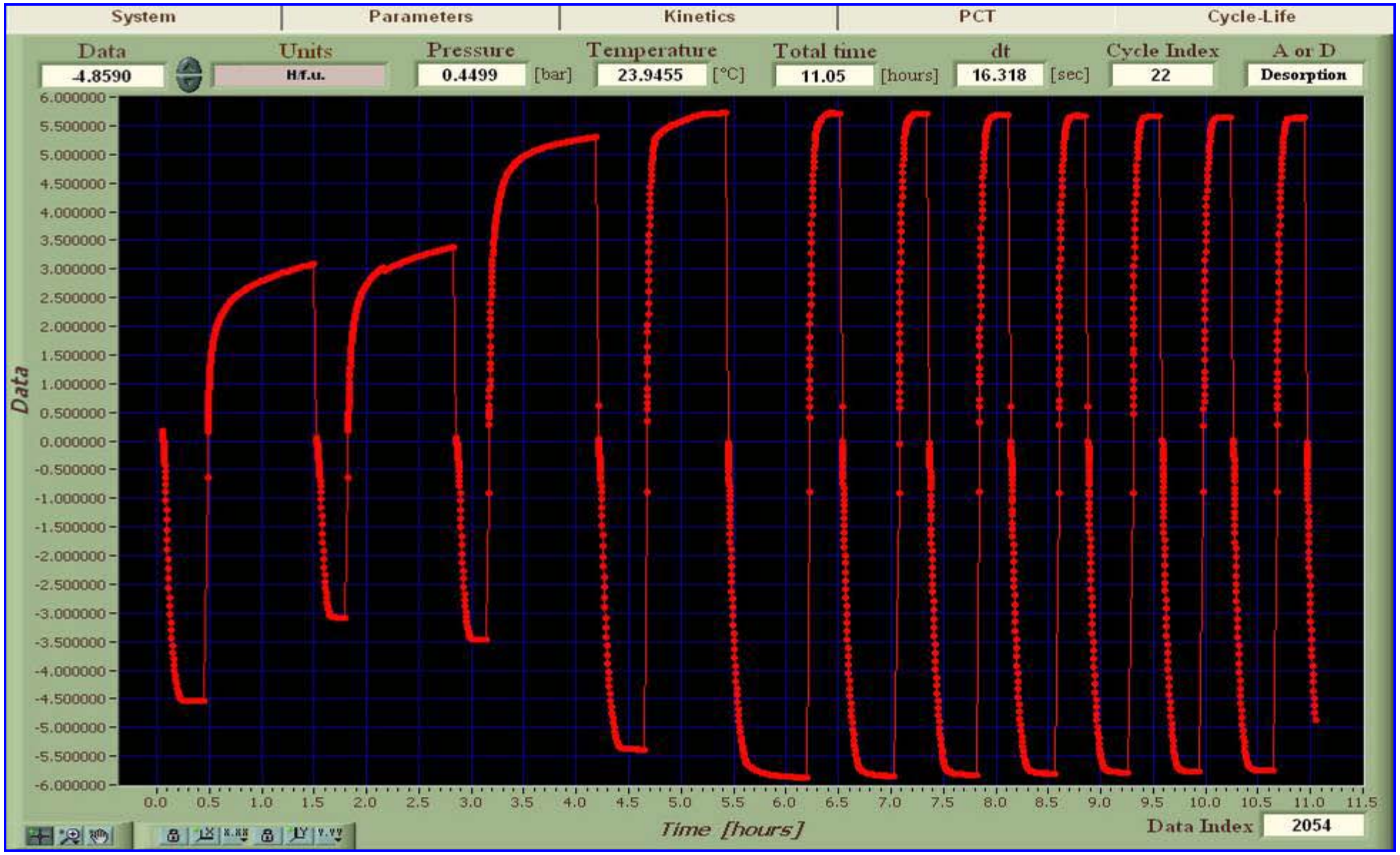


Illustration of how extra free energy due to plastic deformation and the creation of dislocations can lead to hysteresis. The two curves show the change in free energy during each real process. The straight lines represent the tangent to the free energy curve, or the chemical potential. The solid line is the ideal process, the dashed line is for hydrogen absorption and the dotted line is for hydrogen desorption

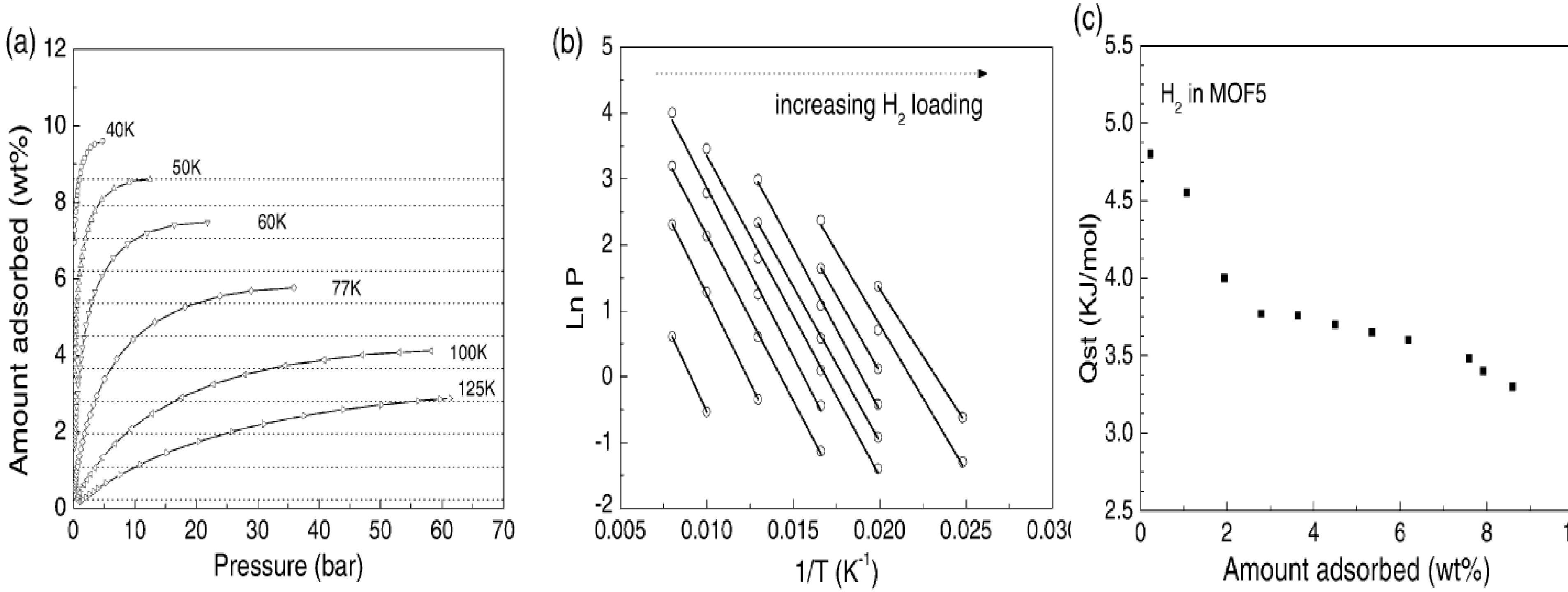
T.B. Flanagan, J.D. Clewley, J. of Less-Common Metals 83 (1982) 127-141

Consideration: Activation - Reversible Hydrides



Example of first activation cycles performed on $LaNi_5$ before making PCT isotherm measurements. Metal hydrides as well as complex hydrides and catalyzed multi-component hydrides generally require activation to reach a stable reversible capacity and performance for a variety of reasons including decrepitation, oxide reduction or penetration, initial irreversible reactions, distribution of reactants and catalysts…..

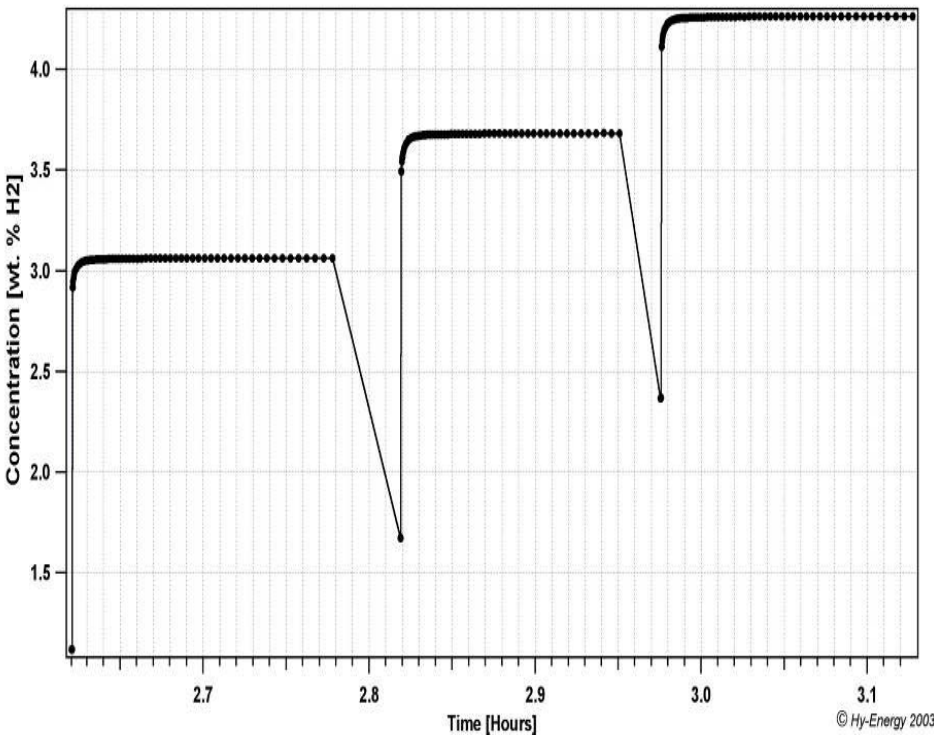
Example: Volumetric PCT Measurements Physisorption Materials

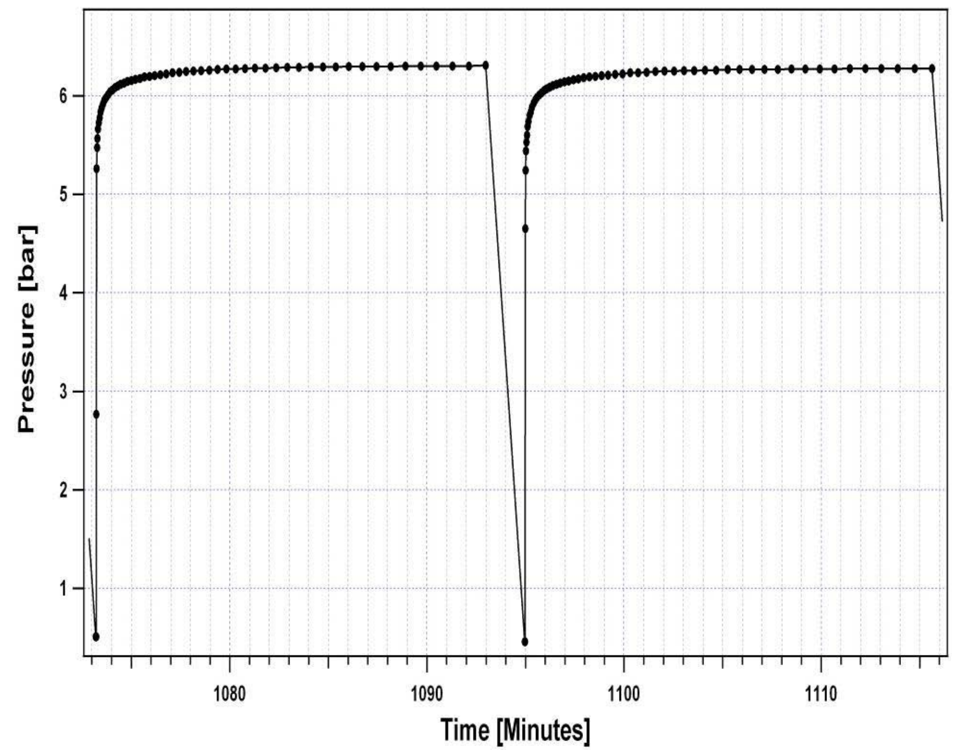


a) Excess adsorption isotherm data of H_2 in MOF-5, used in the heat of adsorption calculation. Dotted lines indicate P-T data at fixed H_2 concentrations. (b) The ln P vs. 1/T plot of H_2 in MOF-5 at various wt.%. (c) Clausius-Claperyron equation: the isoteric heat of adsorption Q_{st} = -slope × R. plotted for H_2 adsorption in MOF-5, as derived from (b).

Zhou, W., Wu, H., Hartman, M. R., Yildirim, Taner "Hydrogen and Methane Adsorption in Metal-Organic Frameworks: A High-Pressure Volumetric Study." J. Phys. Chem. C 111 (2007): 16131-16137.

Considerations: True "Equilibrium" PCT Measurements - Reversible Materials





PCT measurements must allow enough time to reach true "equilibrium" conditions for measured pressures to be used in van't Hoff analysis. Examples of achieving required equilibrium: (left) Concentration vs. time dosing steps for hydrogen desorption from a high-surface area Si-aerogel, (right) pressure vs. time for hydrogen desorption from $LaNi_5$.

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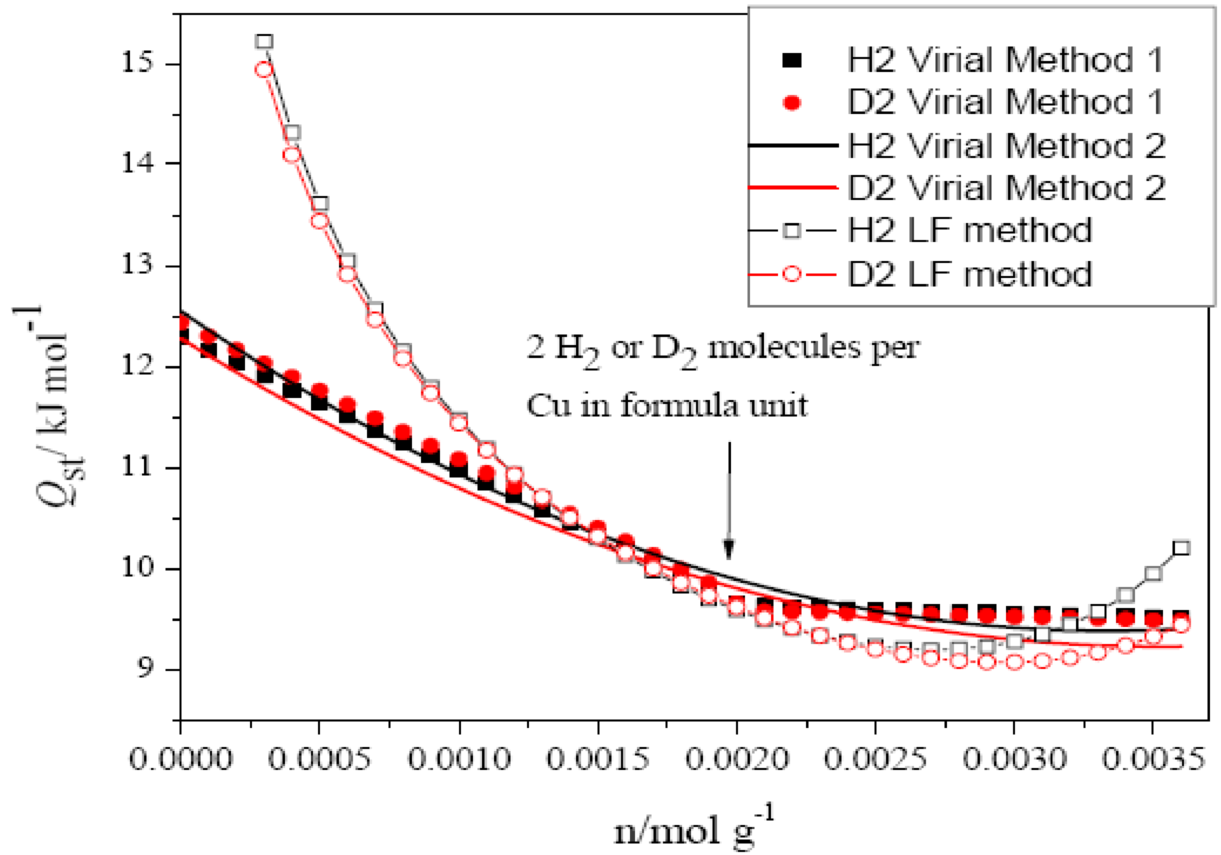
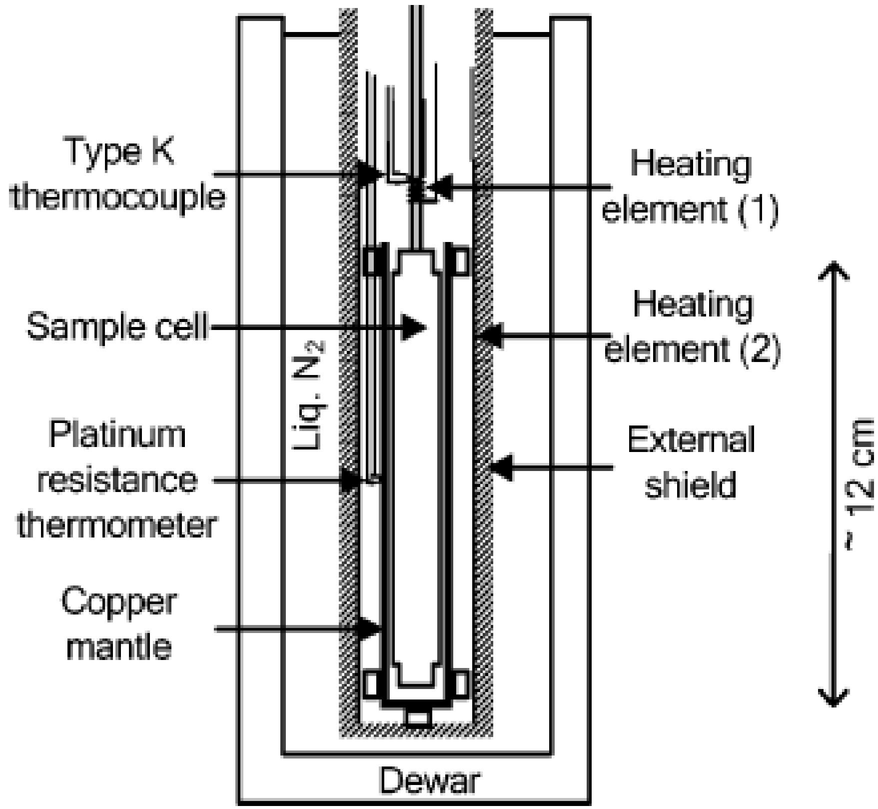
Consideration: Method to Determine Isoteric Heat of Adsorption - Physisorption Materials



Comparison of isosteric enthalpies of adsorption (Qst) calculated using virial methods and Langmuir-Freundlich methods for H2 and D2 adsorption on a MOF material.

Chen, B., Zhao, X., Putkham, A., Hong, K., Lobkovsky, E. B., Hurtado, E. J., Fletcher, A. J., Thomas, K. M. "Surface Interactions and Quantum Kinetic Molecular Sieving for H2 and D2 Adsorption on a Mixed Metal-Organic Framework Material." J. Am. Chem. Soc., 130 (2008): 6411-6423.

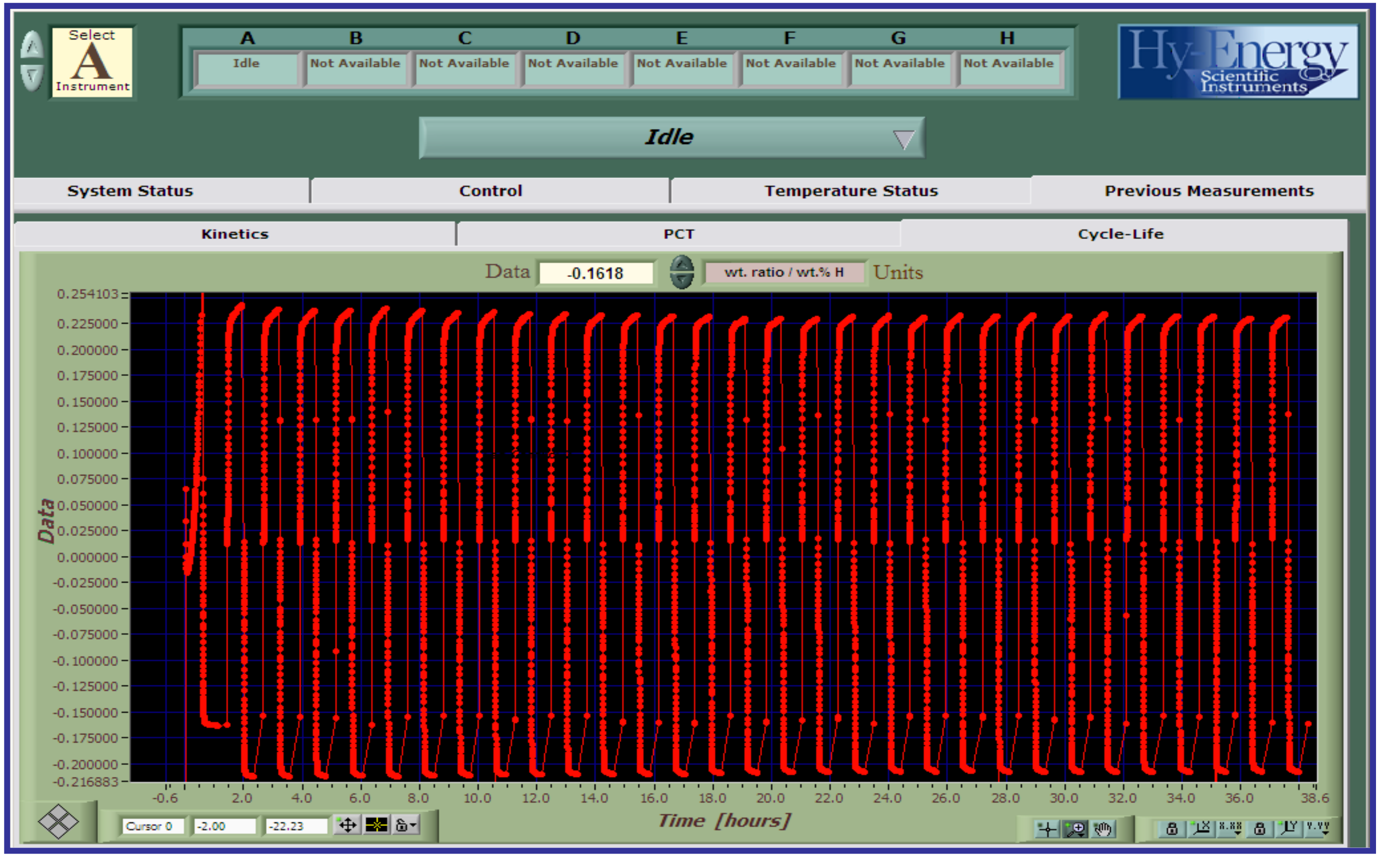
Example Instrumentation: Cryogenic Sample Cell
Volumetric Measurements - Physisorption Materials



Schematic view of a cryostat with a separate gas reheating element to reduce the temperature gradient region of the gas.

Poirier, E., Chahine, R., Benard, P., Lafi, L., Dorval-Douville, G., Chandonia, P. A. "Hydrogen Adsorption Measurements and Modeling on Metal-Organic Frameworks and Single-Walled Carbon Nanotubes." Langmuir 22 (2006): 8784-8789.

Combined Measurements: Gas Sorption + Calorimetry



Instruments:

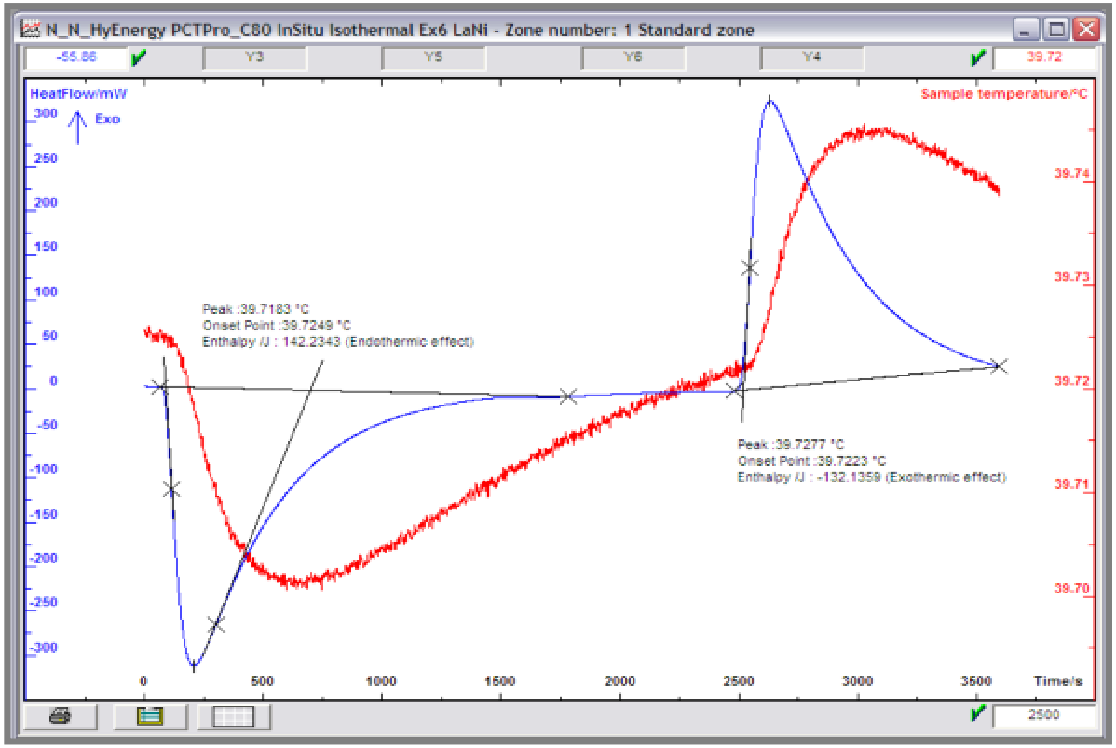
- **Sieverts:** Capacity, Activation and Kinetics.
- **Calorimeter:** Heat of reaction.

Activation Abs/ Desorption cycles

- **Partial activation 1st cycle.**
- **Hydriding steady but incomplete 30+ cycles.**
- **Unusual low capacity, 1/6 of normal.**

Levchenko, A.A., Etherington, G. and Gross, K., "Simultaneous calorimetric and gas sorption measurements provide vital information for developing future hydrogen storage materials", International Gases & Instrumentation Vol. 3, Issue 3, May/June (2009)

Combined Measurements: Gas Sorption + Calorimetry



Calorimetry on cycle 20

- **4.377 gm LaNi5 ↔ 1/6 $LaNi_5H_6$**
- **Measured: 0.004875 moles H_2**
- **ΔH: 142.2 J = 29.2 kJ/mol H_2**

Sample after 32 cycles

- **Many large particles remain**
- **Sieving of fines (hydride) ~ 1/6 by mass**
- **Confirmation: sample only partially reacted**

<u>CAUTION:</u> Necessary to quantitatively measure hydrogen uptake/release and heat transfer simultaneously to get accurate enthalpy of reaction!

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Future Work

• Thermodynamics

- The objective of this task is to establish and review methodologies for determining equilibrium thermodynamics of hydrogen storage materials. In particular, the need to separate true equilibrium conditions from kinetic effects.
- New techniques for rapid determination of thermodynamic stabilities will be presented.
- Final draft of the thermodynamics section will be reviewed by experts in the field and added to the public document.

• Cycle-life Properties

- This task will focus on developing better definitions of how such tests should be performed.
- We will detail what parameters may impact results and what properties are the most critical in performance evaluation (e.g.. capacity fade, or degradation in kinetics…).
- We will complete a draft version of this section for review by the experts

Project Summary

- ***Relevance:*** To fill the need for a best practices guide for the measurement of critical performance properties of advanced hydrogen storage materials.
- ***Approach:*** Create a reference resource of best methods and caveats in measuring Target-based properties: General Introduction to Hydrogen Storage Materials and Measurements, Kinetics, Capacity, Thermodynamic and Cycle Life Measurements.
- ***Accomplishments:*** Task 1, 2, and 3 completed. Task 4 and 5 in progress.

  Achieving a high-level of participation from experts in the field.
- ***Collaborations:*** Official collaboration with NREL, multiple co-authors and International collaboration through IEA task 22 with AIST Japan as well as industry.
- ***Future Work:*** Complete Task 4 (Thermodynamic) and Task 5 (Cycle Life measurements).
- ***Document:***

http://www1.eere.energy.gov/hydrogenandfuelcells/storage/test_analysis.html

Thank You!

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