Best Practices for Characterizing Hydrogen Storage Properties of Materials

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Overview

Timeline

- Start – Feb 2007
- End – Cont.
- 50% complete

Budget

- Total project funding
  - DOE $311K
  - Contractor $64K
- Funding FY07 $161K
- Funding FY08 $150K

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, Review and Contract Management
- University of California Berkeley
- IEA Task 22, Dr. Kuriyama AIST, Japan
- Review by experts: IEA Task 22 & others

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

- 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

- **Milestones FY07:** Draft document of Kinetics section to be delivered to DOE POC by Sept. 30, 2007.
- **Results:** Milestone met June 2, 2007.

- **Go/No-Go FY07:** If the deliverable document has not been completed or is determined to provide no value to the program the project will be terminated (9/07).
- **Decision:** Project to continue with additional tasks.

- **Milestones FY08:** Finalize Kinetics section and prepare drafts of the Introduction and Capacity Sections by Sept. 30, 2008.
- **Results:** Kinetics section completed.
  Introduction and Capacity Sections in progress.

- **Go/No-Go FY08:** If the deliverable document has not been completed or is determined to provide no value to the program the project will be terminated (9/08).

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.

Response to Reviewers Comments

- ***Relevance:*** We are making an effort to include not only information that will be helpful to new researchers entering the field but also details that are important to experienced researchers.

- ***Approach:*** With feedback from the DOE, we have restructured the project into sections including an Introductory section which will also provide background for each of the follow-on sections .

- ***Accomplishments:*** We have received a great deal of edits and feed-back from experts to be incorporate into final documents. This requires time and patience, but I believe we are well on track with our delivery schedule.

- ***Collaborations:*** The IEA HIA task 22 meetings have provided a great venue to present information and to meet one-on-one with experts to encourage their participation in this project.

- ***Future Work:*** Based on comments from last years review, we immediately contacted Dr. Michael Miller of SwRI who provided very substantive edits and comments which have been incorporated in the Kinetics and Introduction documents.

Key Accomplishments

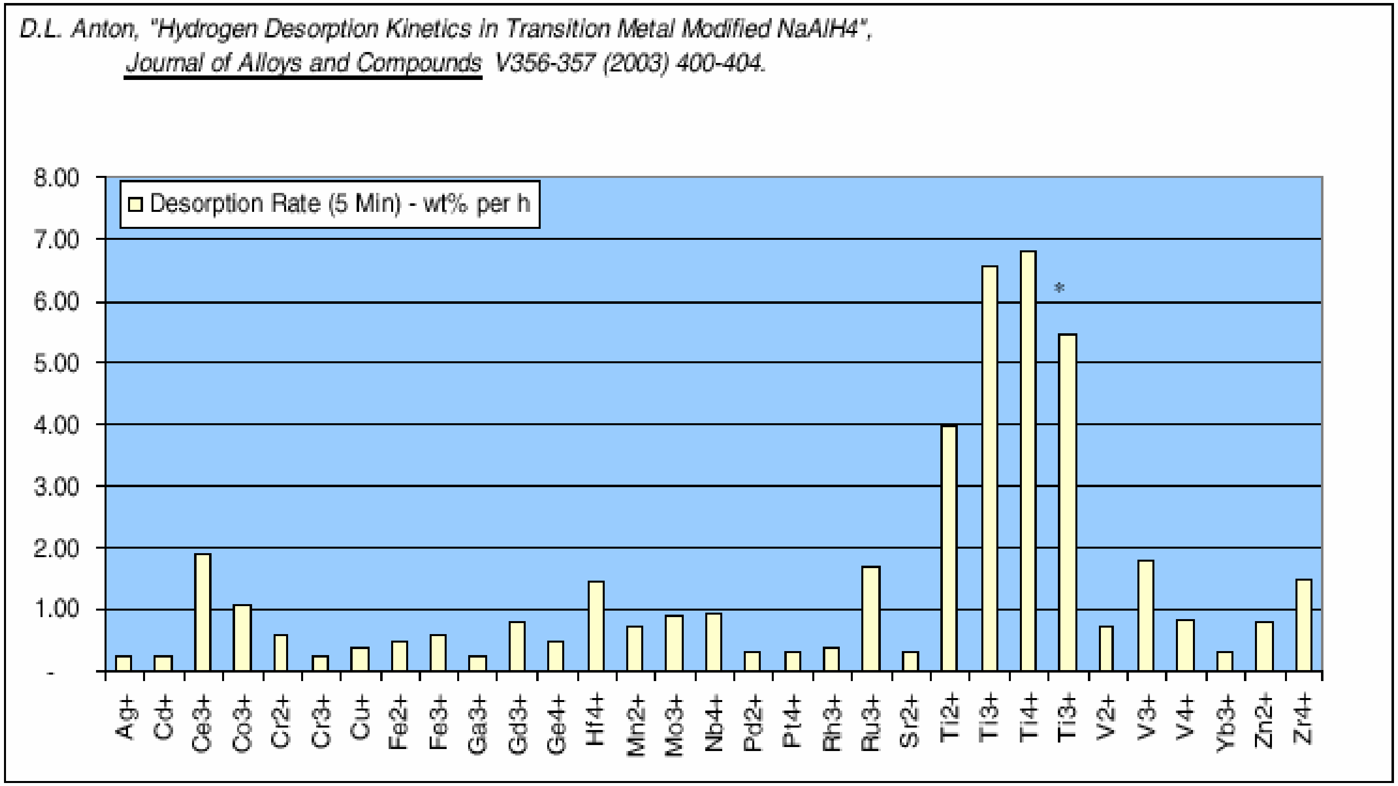
- ***Task 2: Final Kinetics document 100% complete***
  - Compiled examples from the literature and performed example measurements to illustrate key issues associated kinetics and other measurements.
  - Participation as project H-27 “International standardized testing practices for hydrogen storage materials” IEA Task 22 Expert Workshop
  - Contributions and editorial reviews have been received from world experts including:
    - Dr. Philip Parilla of the National Renewable Energy Laboratory in Golden CO,
    - Dr. Gary Sandrock and Dr. George Thomas of the U.S. Department of Energy
    - Dr. Michael Miller of Southwest Research Institute in San Antonio TX
    - Dr. Frederick Pinkerton of General Motors GM R&D Center
    - Dr. Ole Martin Løvvik of the Institute for Energy Technology in Kjeller Norway
    - Professor Channing Ahn of the California Institute of Technology in Pasadena CA
    - Professor Sam Mao of the University of California Berkeley in Berkeley CA
    - Dr. Nobuhiro Kuriyama and Dr. Tetsu Kiyobayashi of the National Institute of Advanced Industrial Science and Technology in Osaka Japan
  - Rough Draft Submitted to DOE June 2007.
  - Final Reviewed Document Delivered to DOE May 2008.
  - Document Posted to DOE website.

Input from Technical Reviewers

- ***Organization:*** The first draft was not organized in a way that made it easy for the reader find topics of interest. The entire document was reorganized with a more clear structure and indexing system.
- ***Introduction:*** It was requested that a more comprehensive introduction be included. Rather than stand-alone sections with their own limited prefaces (sometimes redundant), we are creating a more expansive introduction for the entire document.
- ***Methods:*** It was suggested that we cover a wider range of measurement techniques. This is being included in the introduction section.
- ***Technical:*** A large amount of technical feedback was introduced into the documents, especially from the reviewer's own experimental experiences.

Examples: Task 2 Kinetics

Purpose: Kinetics for Materials Improvement



- **Comparative measurements to evaluate additives.**
- **Sample sizes and conditions must be identical.**
- **There may be effects from other properties: particle size....**

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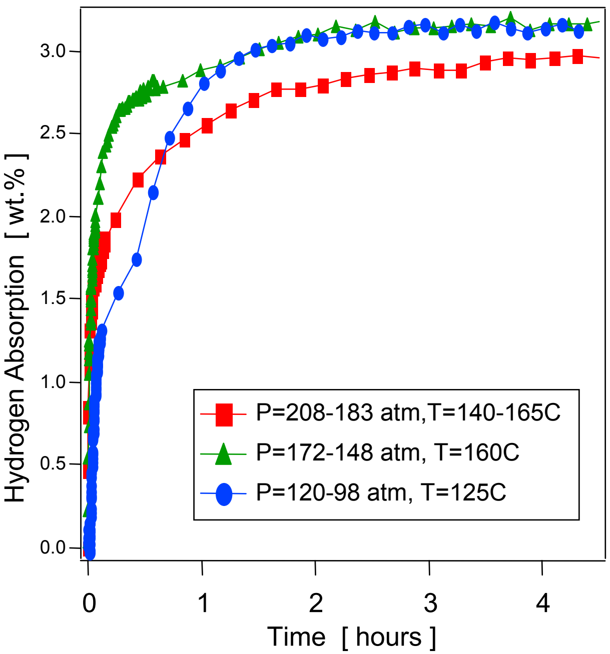
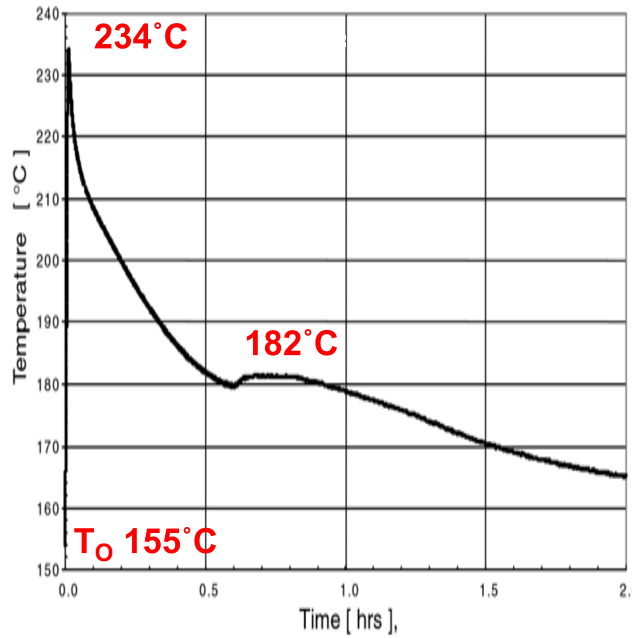
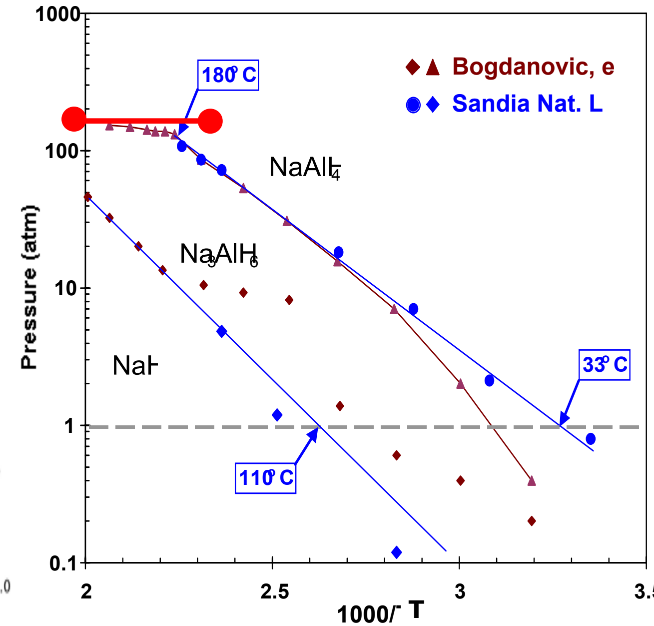
Purpose: Engineering Kinetics Measurements







100g Scaleup Bed Ti/Zr-Alkoxide Doped $NaAlH_4$

- **Rapid charging produces large ΔH heating effects**
- **Reaction enthalpy can melt $NaAlH_4$ (182˚C)**
- **Temperature measurements shows self-melting and resolidification**
- **Sorption kinetics affected by heat transfer**

Gary Sandrock, Presentation MH2000 October 1-6, 2000 - Noosa, Australia

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Purpose: Fundamental - Kinetic Mechanisms

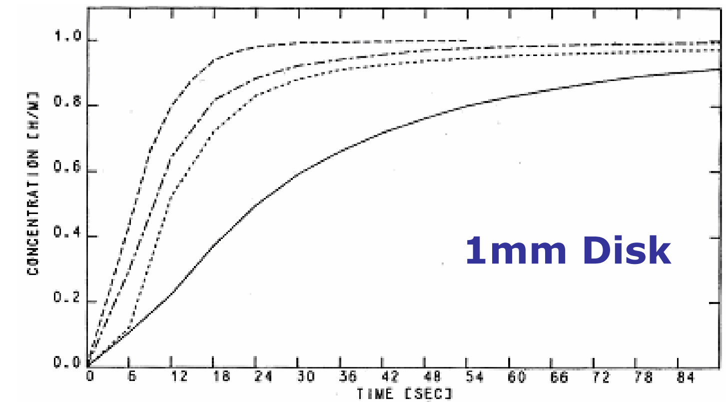


Fig. 3. Absorption reaction rates for $LaNi_{4.7}Al_{0.3}$ (bed thickness, 1 mm; distance from equilibrium, 2 bar): ——, 293 K; - - - -, 303 K; — · —, 313 K; — — —, 323 K.

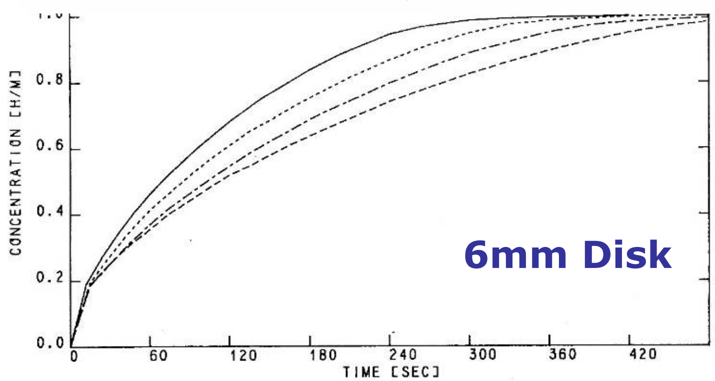
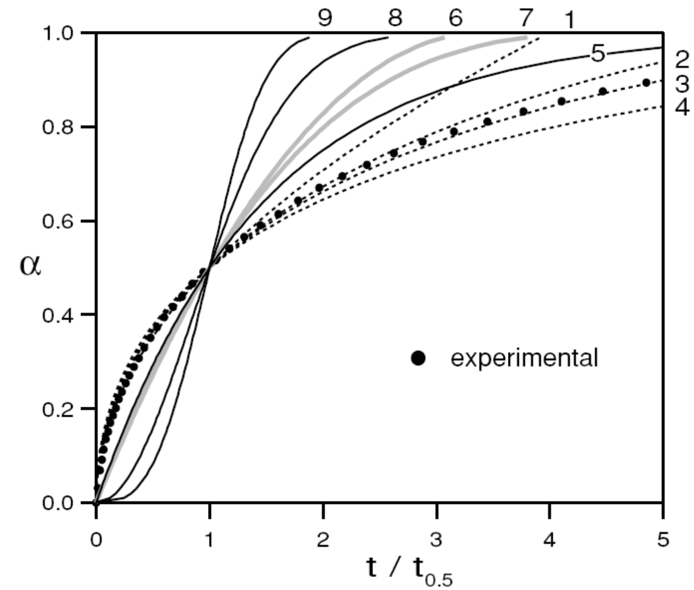


Fig. 6. Absorption reaction rates for $LaNi_{4.7}Al_{0.3}$ (bed thickness, 6 mm; distance from equilibrium, 2 bar): ——, 293 K; - - - -, 303 K; — · —, 313 K; — — —, 323 K.



Kinetics curves based on different solid state kinetics models

- **Caveat for interpreting experimental measurements: Kinetics behavior is dominated by heat transfer making the determination of rate limiting mechanisms difficult to impossible without good experimental design.**

Rudman, P.S. "Hydriding and Dehydriding Kinetics." Journal of the Less-Common Metals, 89 (1983): 93-110. / Supper, W., Groll, M., Mayer, U. Journal of the Less-Common Metals, 104 (1984): 279-286. Sharp, J. H., Brindley, G. W., Narahari-Achar, B. N., J. Am. Ceram. Soc., 49 (1966) 379.

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New Task 1: General Introduction

1.1 Purpose of Measurements

- Materials Development, System Performance, Fundamental Science

1.2 Basic Description of Hydrogen Storage Properties

- Capacity, Kinetics, Thermodynamics, Cycle-Life

1.3 Types of Measurement

- Kinetics, Pressure-Composition Isotherm

1.4 Hydrogen Storage Measurements: Directly Measureable Quantities

- Weight, Pressure, Temperature, Cycle, Time
- Accuracy and Precision of Measurements
- Analog to Digital Conversion Error
- Error Bars in Data Representation

1.5 Static and Dynamic Measurements

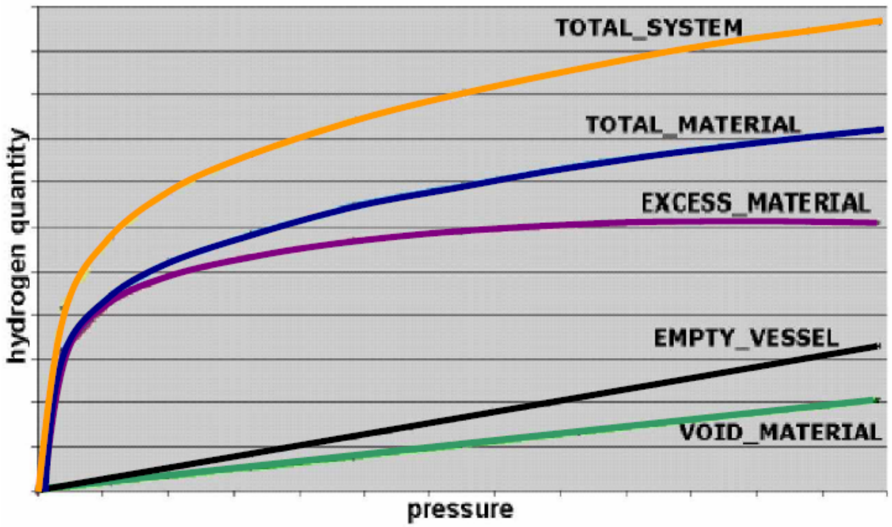
- dC and dP Dosing Methods

1.6 Methods of Measurement

- Volumetric Method - Consideration: Direct vs. Differential Pressure Method, Temperature Correction, Compressibility Factor, Gas Impurities, Instrument Temperature, Leaks, Reverse Joule-Thompson Heating, Sample Size, Skeletal Density, Volume Calibration, Volume Dilatation
- Gravimetric Method - Considerations:Buoyancy, Gas Impurities, Heat Transfer, Leaks, Sample Transfer, Volume Dilatation, Thermal Gradients
- Temperature-Programmed Desorption Method
- Differential Scanning Calorimetry Method
- Thermal Gravimetric Analysis Method

Universal Definitions Needed

- **Stringent Definition of Storage Capacity Needed**
  Confusion even caused on a materials level:
  Total, Absolute, Excess, Vessel values sometimes not properly defined
- **In Materials Science, Excess Capacity Should be Used**
- **On an Engineering Level, Vessel Values Should be Used**
  Total storage capacity of an Empty Vessel vs a Filled Vessel should be evaluated



Volumetric Methods:

Void H_2: Hydrogen being present in the macropores of the high-surface material (calculated using skeletal density)

Excess adsorption H_2 : Quantity of hydrogen adsorbed on the adsorber (calculated using skeletal density)

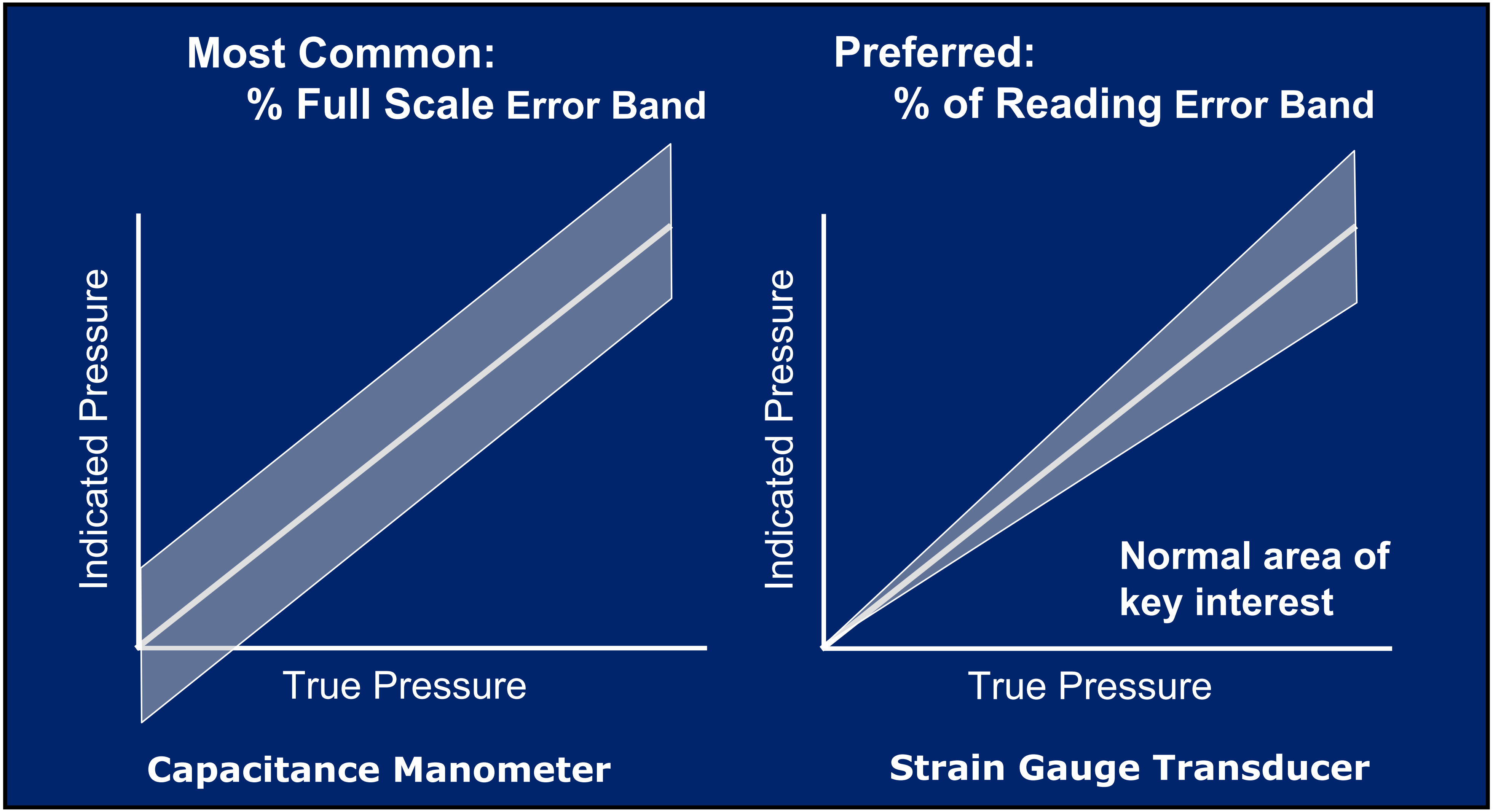
Total material H_2: Total amount of hydrogen being stored by the high-surface material

- **Importance of the Volumetric Storage Density of the Adsorber**
  Apparent density of the storage material should always be measured

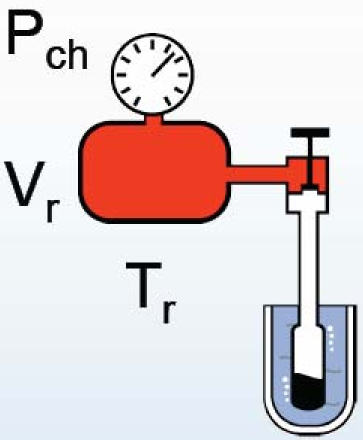
Volume change with state of charge should be accounted for

Taken from presentation by: Dr. Ulrich Eberle, Adam Opel AG "GM Fuel Cell Activities"
WE-Heraeus-Seminar – October 2005, Bad Honnef, Germany

Accuracy: Example - Pressure Transducers

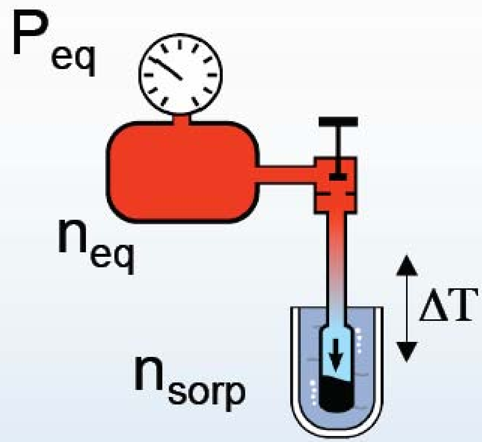


Temperature Corrections: Volumetric Method

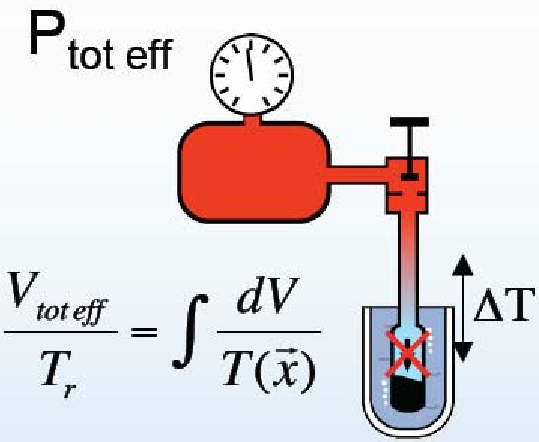


Charge a calibrated volume at a controlled temperature to a measured pressure

$$n_{ch} = \frac{P_{ch} V_r}{R T_r}$$



Expand gas into sample vessel volume, let equilibrate and measure pressure



$$\frac{V_{tot\,eff}}{T_r} = \int \frac{dV}{T(\vec{x})}$$

Determine <u>effective</u> total volume using either a non-absorbing gas and/or sample.

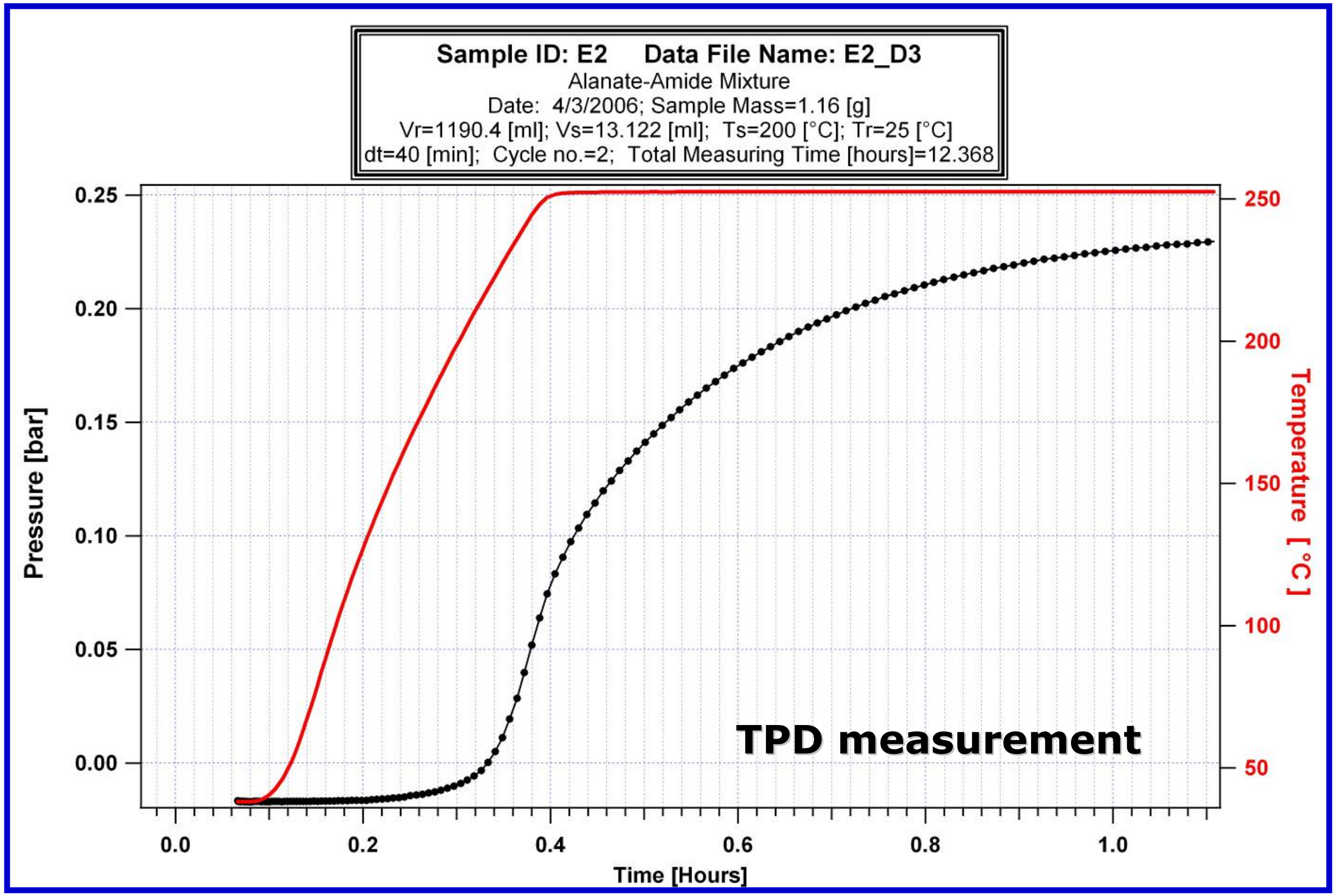
Define:

$$\gamma \equiv \frac{V_r}{V_{tot\,eff}} = \frac{P_{tot\,eff}}{P_{ch}}$$

NREL National Renewable Energy Laboratory

Example: Today's Materials - Complex systems!

Alanate–Amide mixtures



- **One or multiple reactions ?**
- **Only Hydrogen released ?**

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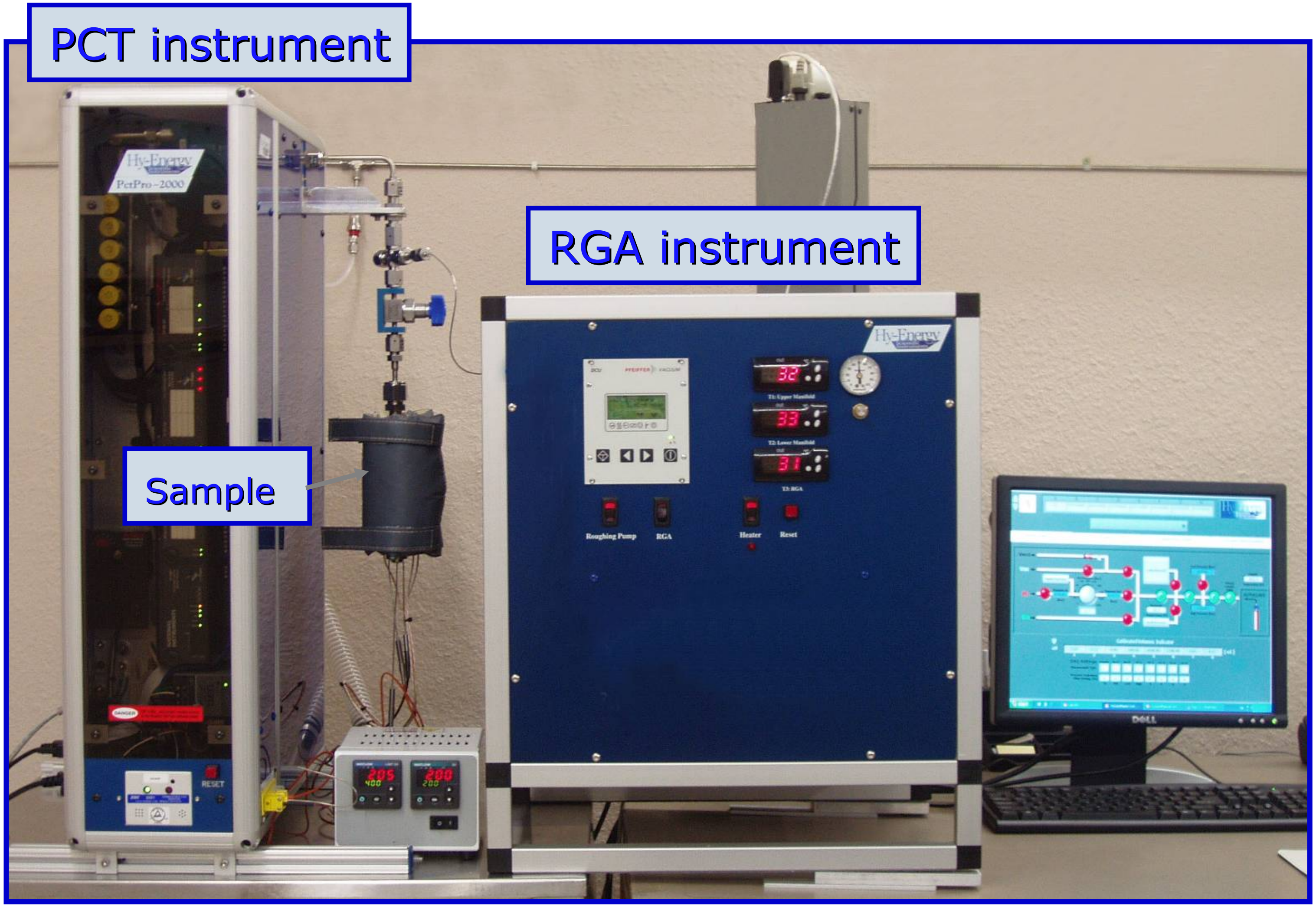
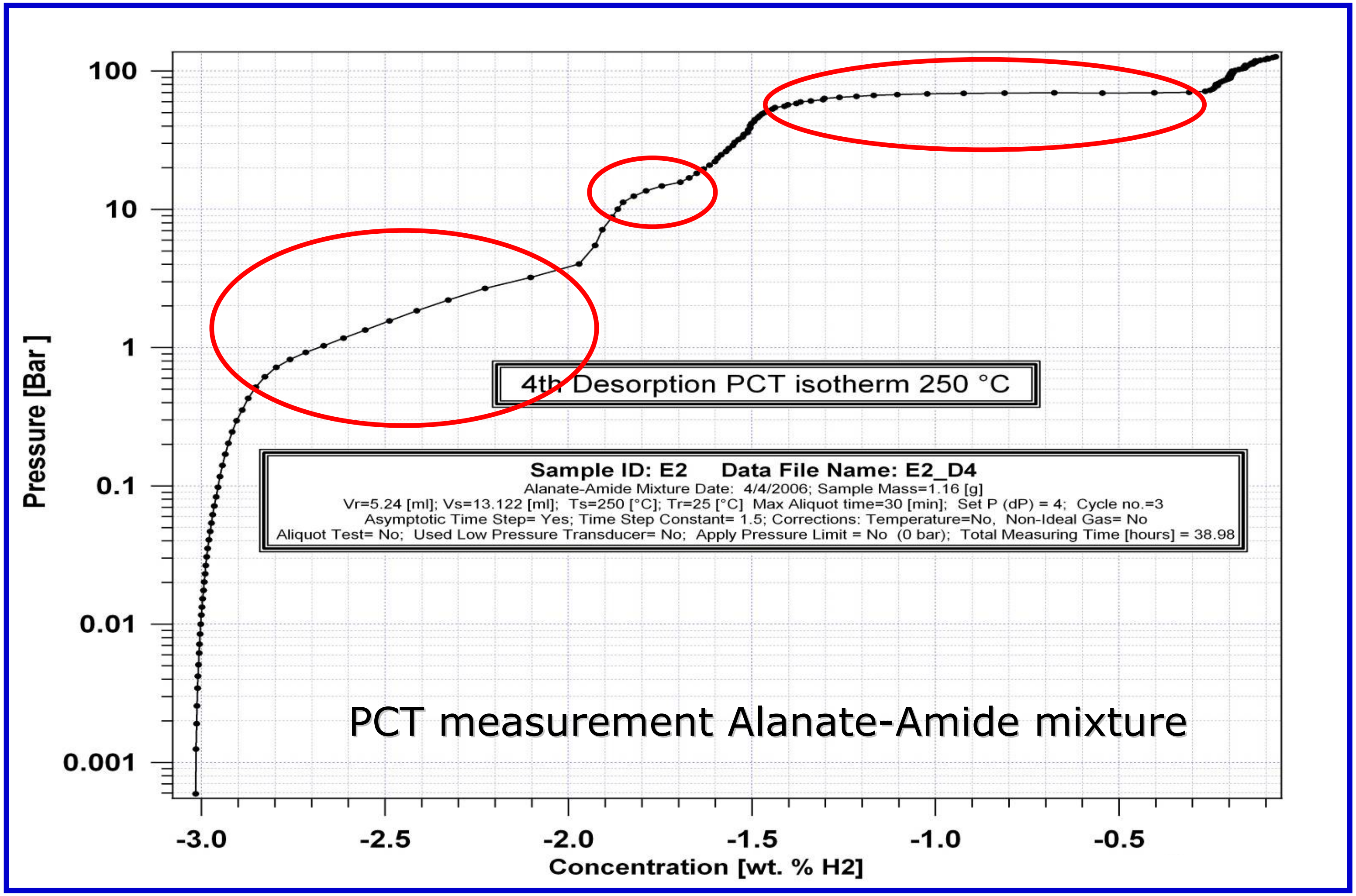
Simultaneous Measurements

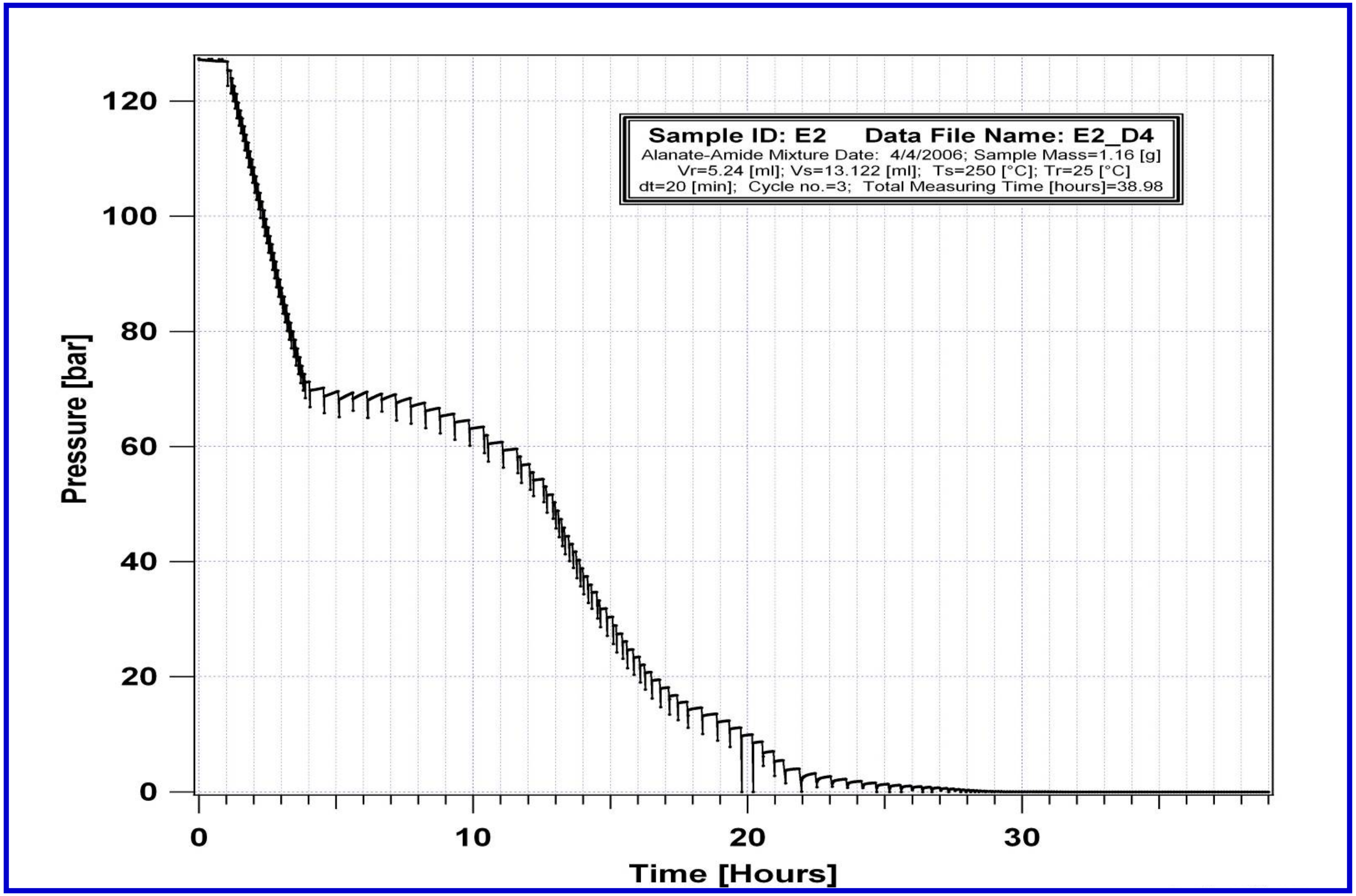


- **Desorbed gas: Hydrogen only or side reactions?**
- **In situ RGA: real-time gas composition analysis**



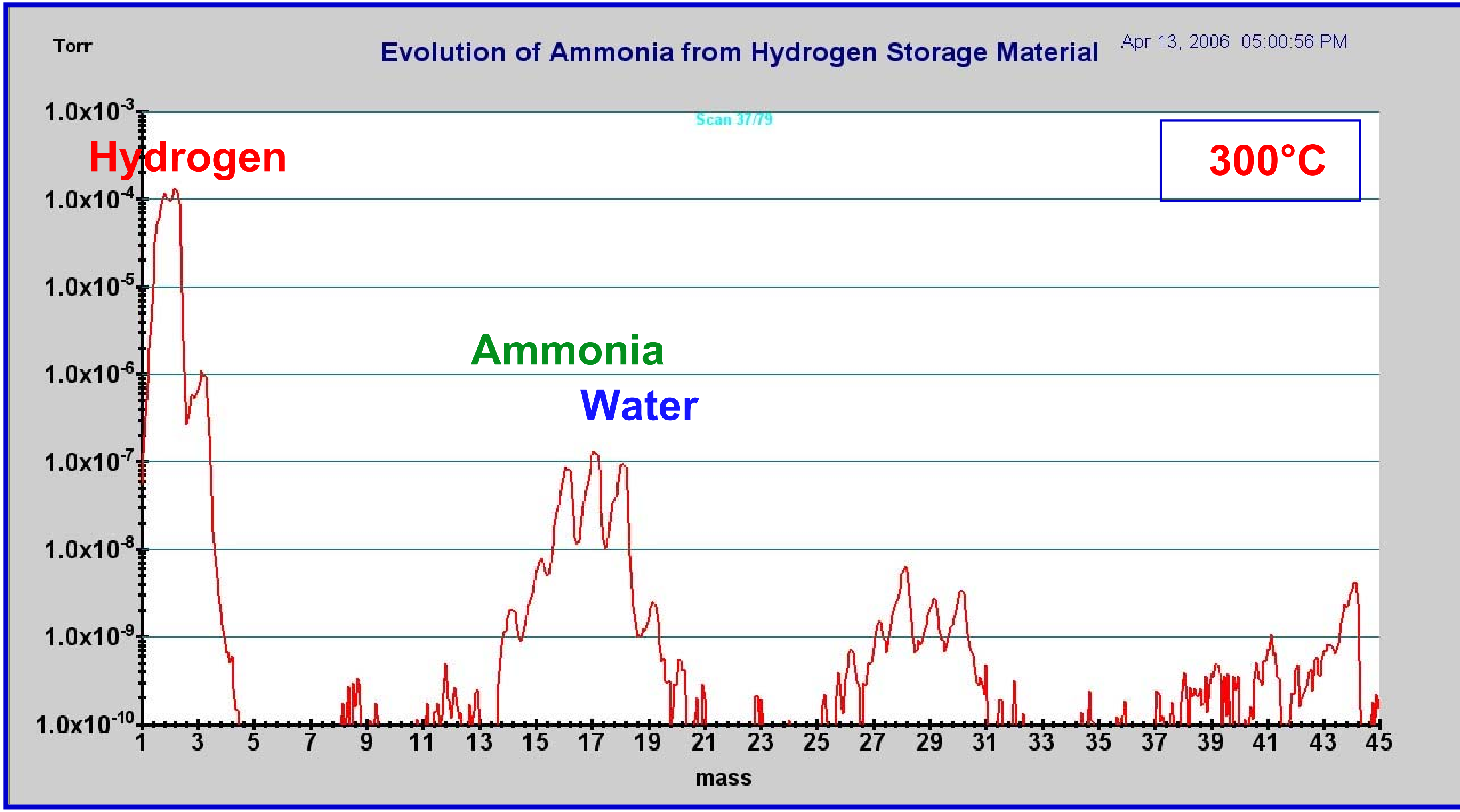
- **Multiple reactions apparent**
- **Wide range of Thermodynamic Stability**
- **Each contributes to total observed kinetics**

PCT measurement Alanate-Amide mixture



- **Kinetics of each reaction can be measured independently**

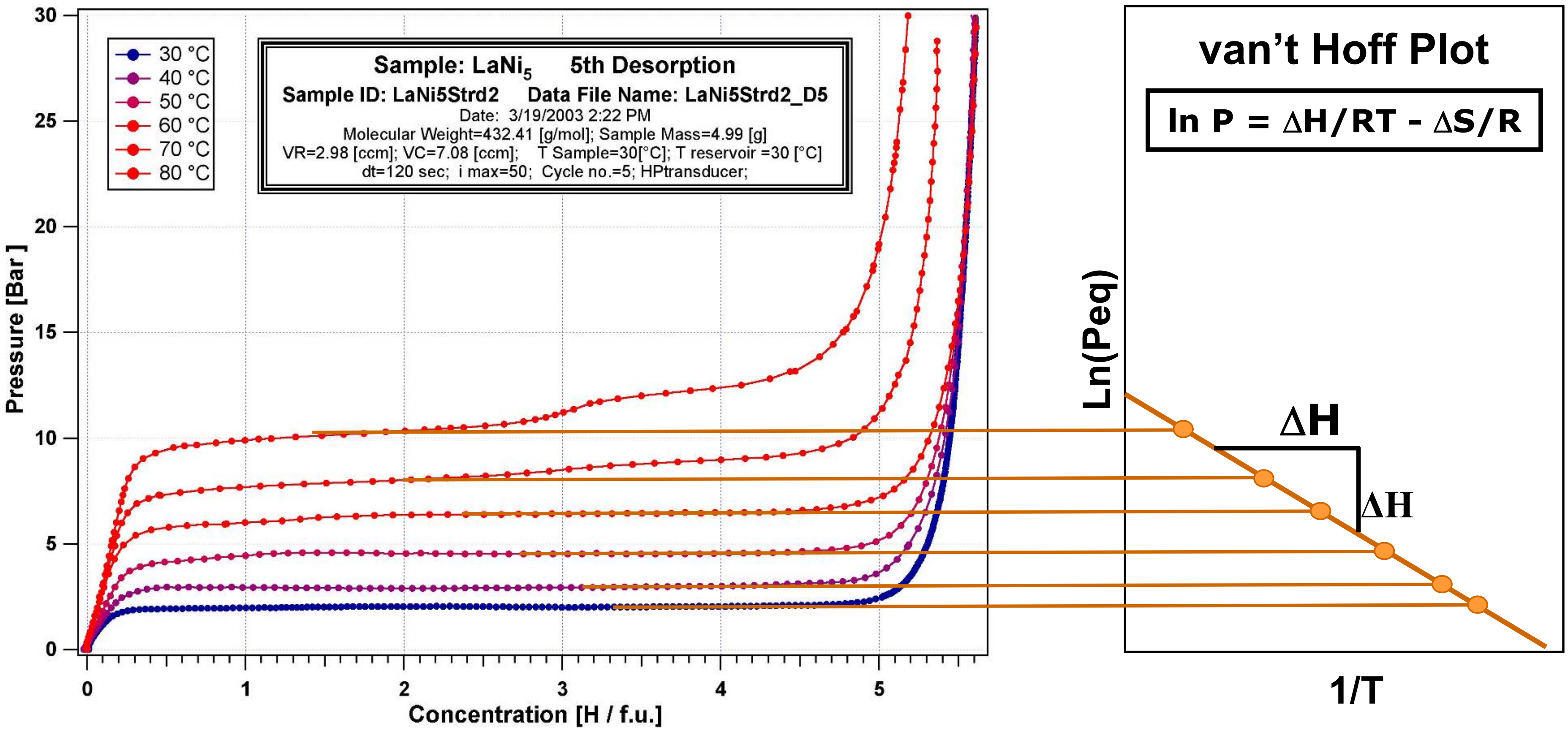
In Situ Residual Gas Analysis



- **Alanate-Amide mixture:**

  Ammonia appears to be released during hydrogen desorption

Efficiency: PCT Measurements - Thermodynamic Properties



- Thermodynamics typically from series of isotherms
- Time consuming !

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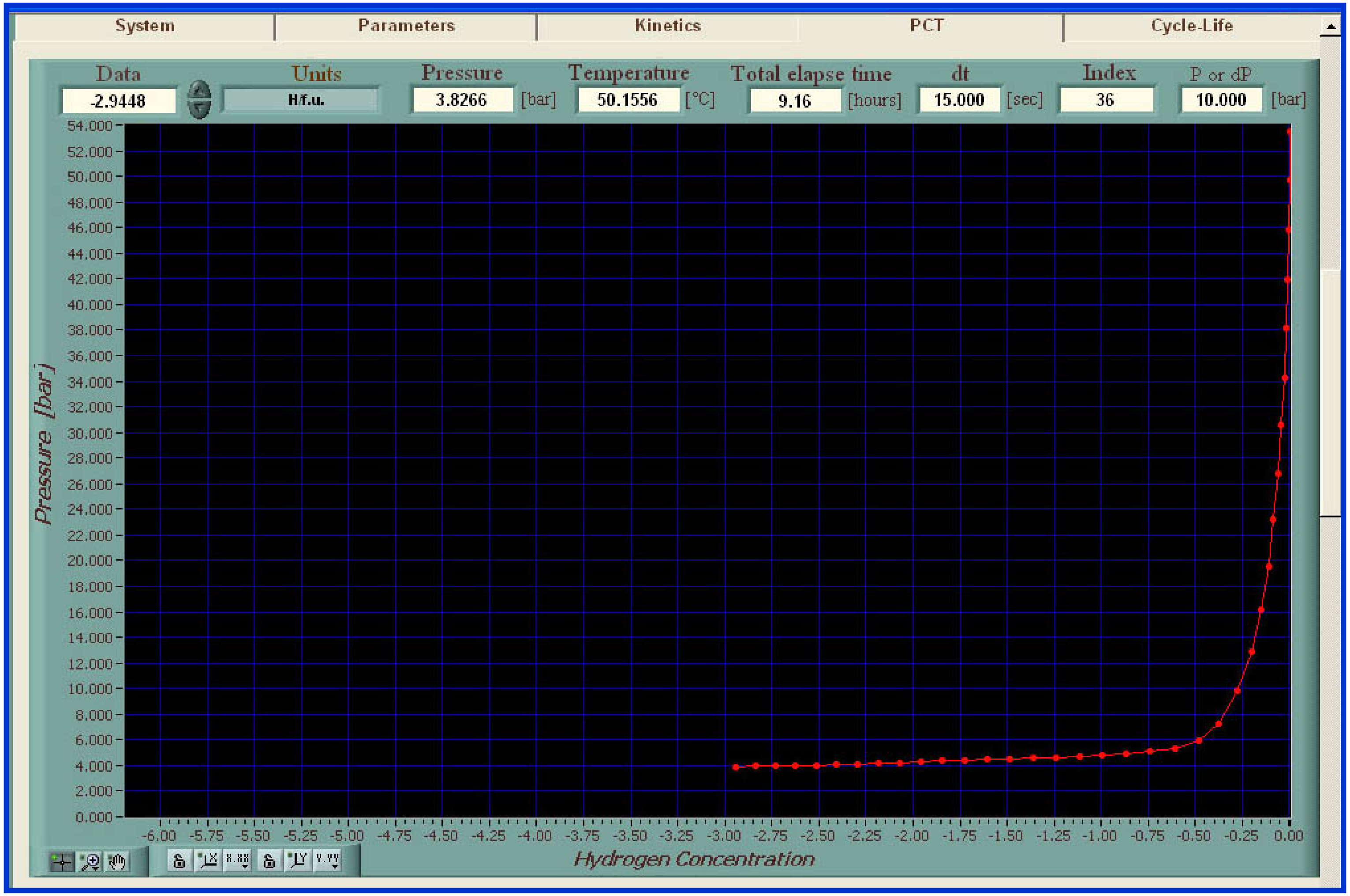
Thermodynamics: The Hy-Energy Method

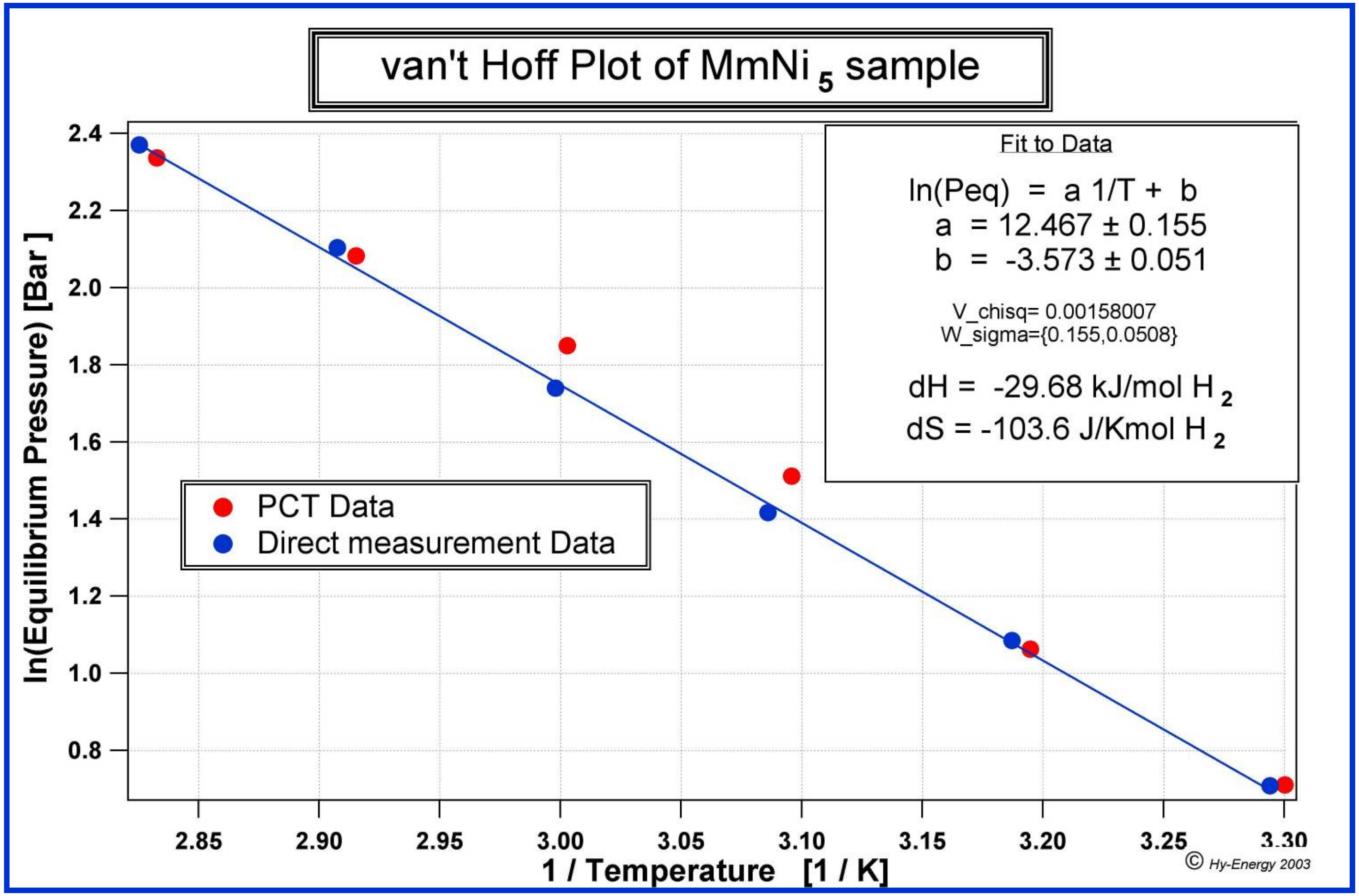


- Direct van't Hoff measurement
- PCT measurement to specific (mid) composition

Pressure v.s. Time Profile

- Change time limit for aliquot
- Increase temperature in steps

van't Hoff Plot



- Classically derived from series of PCT measurements
- Specially designed instruments can determine thermodynamics in a Quick single direct measurement

Collaborations

- **Contributions to this project from world experts have been received including written materials, examples, presentation or editorial review of draft documents from:**
  - **Dr. Philip Parilla, 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 and Russell Carrington, University of California Berkeley**
  - **Dr. Michael Miller of Southwest Research Institute in San Antonio TX**
  - **Dr. Frederick Pinkerton of General Motors GM R&D Center**
  - **Professor Channing Ahn, California Institute of Technology, USA , 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.**

Future Work

- ***General Introduction***
  - Complete review and deliver of final version of Introduction section to DOE Sept FY08
- ***Capacity***
  - Hydrogen storage capacity is key metric for practical hydrogen storage.
  - It is critical that capacity measurements are performed with a clear understanding of commonly encountered caveats and pitfalls.
  - Complete deliver of draft version of Capacity section to DOE September FY08.
  - Complete deliver of final version of Capacity section to DOE January FY09.
- ***Thermodynamics***
  - The objective of this task is to establish methodologies for determining equilibrium thermodynamics of hydrogen storage materials.
  - We will define protocols to separate true equilibrium conditions from kinetic effects.
  - We will examine details of new techniques for rapid determination of thermodynamic stabilities.
  - Complete deliver of Final version of Thermodynamic section to DOE September FY09.
- ***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…).
  - Complete deliver of Final version of Thermodynamic section to DOE September FY09.

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: Kinetics, Capacity, Thermodynamic and Cycle Life.
- ***Accomplishments:*** Task 1 approaching completion. Task 2 completed.

  Achieving a high-level of participation from experts in the field.
- ***Collaborations:*** Official collaboration with NREL and International collaboration through IEA task 22 with AIST Japan as well as industry.
- ***Future Work:*** Complete Task 1: General Introduction. Continue work on Tasks 2-4 Introduction, Capacity, Thermodynamic and Cycle Life measurements.
- ***Document:***

  http://www1.eere.energy.gov/hydrogenandfuelcells/hydrogen_publications.html#h2_storage

Thank You!

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