NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Hydrogen Sorbent Measurement Qualification and Characterization

Philip Parilla
National Renewable Energy Laboratory
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Overview

Timeline*

Start: October 2012
End: to be determined
% complete FY 15: ~65%

*previously a component of NREL's materials development program and supported annually since 2006

Budget

Funding FY15: $510k
Funding FY14: $400k
Total Project Funding: N/A

Barriers addressed

General: A. Cost, B. Weight and Volume, C. Efficiency, E. Refueling Time

Reversible Solid-State Material:
- M. Hydrogen Capacity and Reversibility
- N. Understanding of Hydrogen Physi- and Chemisorption
- O. Test Protocols and Evaluation Facilities

Collaborators

H2Technology Consulting, USA – Karl Gross

TAMU, USA – Joe Zhou group

UCSD, USA – Seth Cohen group

H_2ST^2, USA – Hydrogen Storage Tech Team

NIST, Facility for Adsorbent Characterization and Testing (FACT) – ARPA-E Project

LANL, USA – Troy Semelsberger

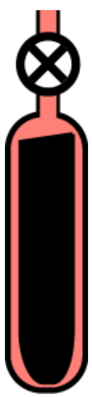
Outline: Three Research Activity Areas

- **Volumetric Capacity Protocols**
  - Develop recommended measurement and analysis protocols
  - Disseminate results to storage community
- **Thermal Conductivity Measurements for H_2 Storage Materials**
  - Develop measurement hardware & procedures
  - Measure at variable temperatures and gas pressures
  - Validate measurements using known materials
- **Verification and Error Analysis for H_2 Capacity Measurements**
  - Independently measure capacities to verify claims
  - Assist community to minimize measurement errors

Relevance: Volumetric Capacity Protocols

DOE Objective:

Volumetric capacity metrics are critical for technological and commercial development; they must be calculated and reported in a uniform and consistent manner to allow comparisons among different materials. There needs to be a uniform protocol for determining and reporting on volumetric capacity.



Project Goals:

Develop Volumetric Capacity Protocols

- Compile a complete list of volumetric capacity definitions and options needed to develop a standardized methodology to measure, calculate, interpret and report on volumetric capacity.
- Propose protocols for the determination of volumetric capacity of sorbent materials. Show that any double counting is prevented.
- Submit a report that will be disseminated to the scientific community.

Relevance: Importance of Volumetric Capacity

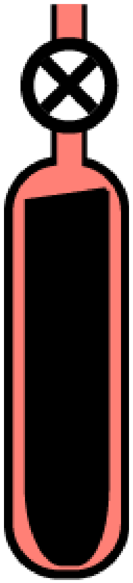
- **Volumetric Capacity (VC) is a crucial figure of merit (FOM) to evaluate H_2 storage materials.**
- **Need standardized and well-defined VC definitions and protocols to provide uniform practices.**
- **We have explored and clarified VC conventions and protocols resulting in guidelines for VC implementations.**
- **We solicited external participation (IEA and H_2ST^2) to ensure a careful & comprehensive implementation.**

Approach: Addressing the Issues

- **Conventions**
  - Accounting for hydrogen
    (Accurate counting! No double counting.)
  - Accounting for volumes
  - Best FOM for a given situation
- **Measurement Protocols**
  - Implementing the conventions into practice
  - Ancillary protocols (e.g., bulk & skeletal densities)
- **Sample Preparation**
  - Standard preparation (degassing, activating)
  - Sample compaction/densification

$$\Lambda_{VC} = \sum_i m_{i\,H_2} \Big/ \sum_i V_i$$

g H_2/L

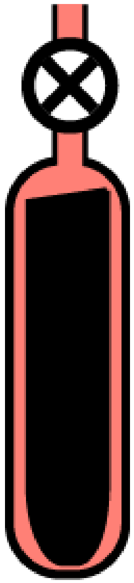


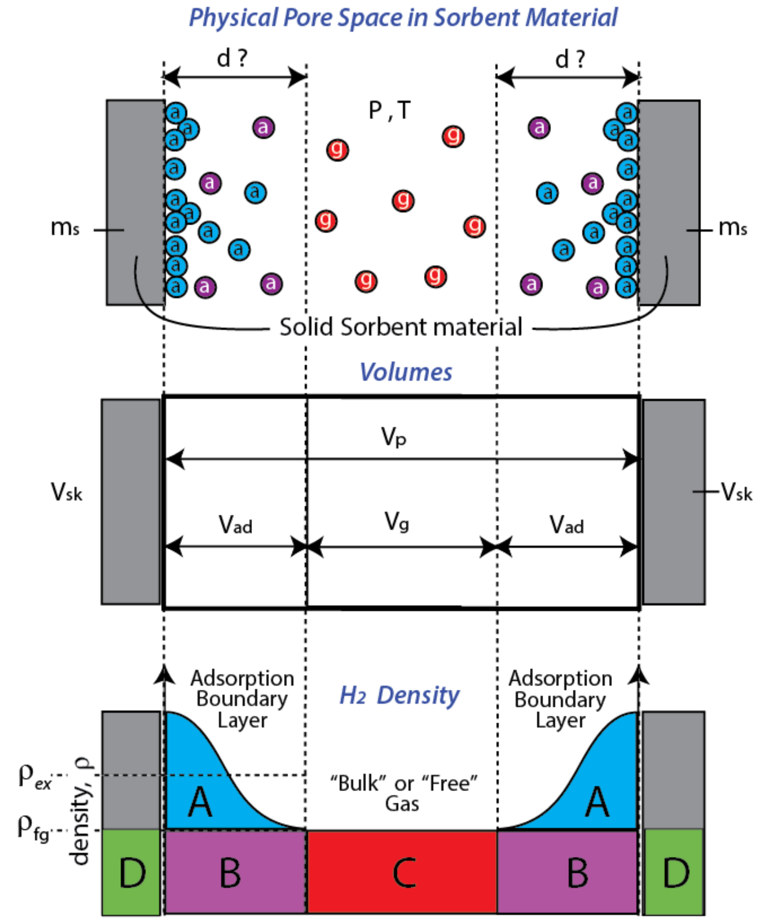
Approach: Accounting for the Hydrogen

Different ways to count H_2:
Excess, Net, Absolute, Total

$$\Lambda_{VC} = \sum_i m_{i\,H_2} \Big/ \sum_i V_i$$

Critical To Not Double-Count the Hydrogen!!!





TERMINOLOGY
Material "Excess" Capacity = (A)
Material "Net" Capacity = (A-D)
Material "Absolute" Capacity = (A+B)
Material "Total" Capacity = (A+B+C)

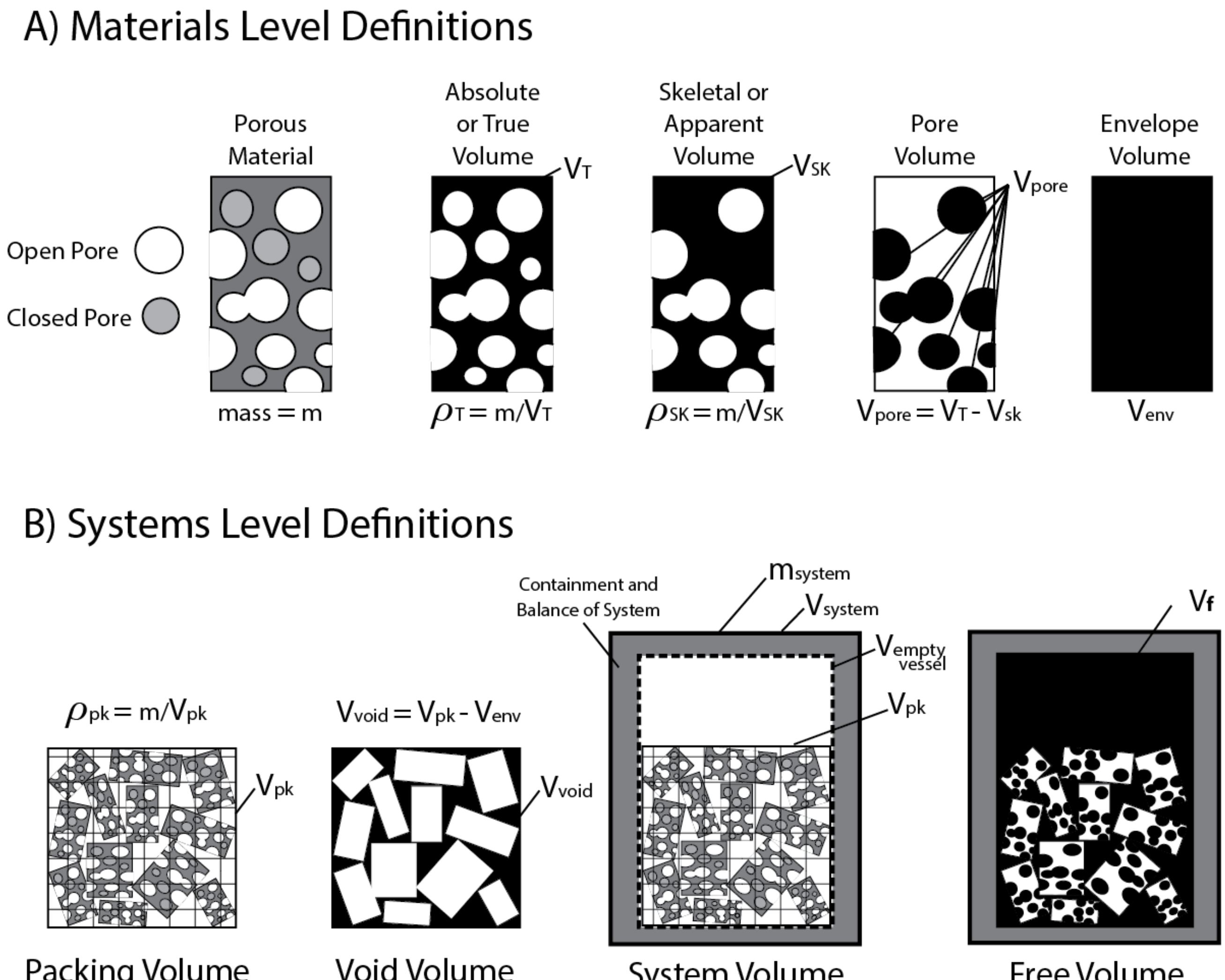
Adapted from Best Practices, K. Gross

Approach: Defining & Accounting for the Volumes

There are various types of volumes to consider

- It is critical that the volume chosen for a FOM can actually be determined in practice!

- The methodology for determining that volume must be explicitly specified.



Adapted from Fig. 84 of Best Practices, K. Gross

For more detail see: http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/best_practices_hydrogen_storage.pdf

Accomplishments: Best FOM for a Given Situation

- **Tailor volumetric capacity FOM to target specific goals**
  - Material evaluation, comparison and optimization
  - Engineering considerations and system optimization

- **Seven FOMs were identified as being useful *and* well-defined**
  - Which one to use depends on material type and goals; can be used for both adsorption and absorption materials.
  - Each FOM can be calculated easily from the same isotherm data sets so it is feasible to report on all seven.
  - Protocols proven to not double count hydrogen for Sieverts and gravimetric methodologies.
  - **FOMs based on <u>absolute capacity</u> are NOT recommended as the absolute adsorption volume is not well-defined.**
  - First draft of report being reviewed by partners and collaborators.

Accomplishments: Seven Volumetric Capacity FOMs

Recommended Volumetric Capacity FOMs

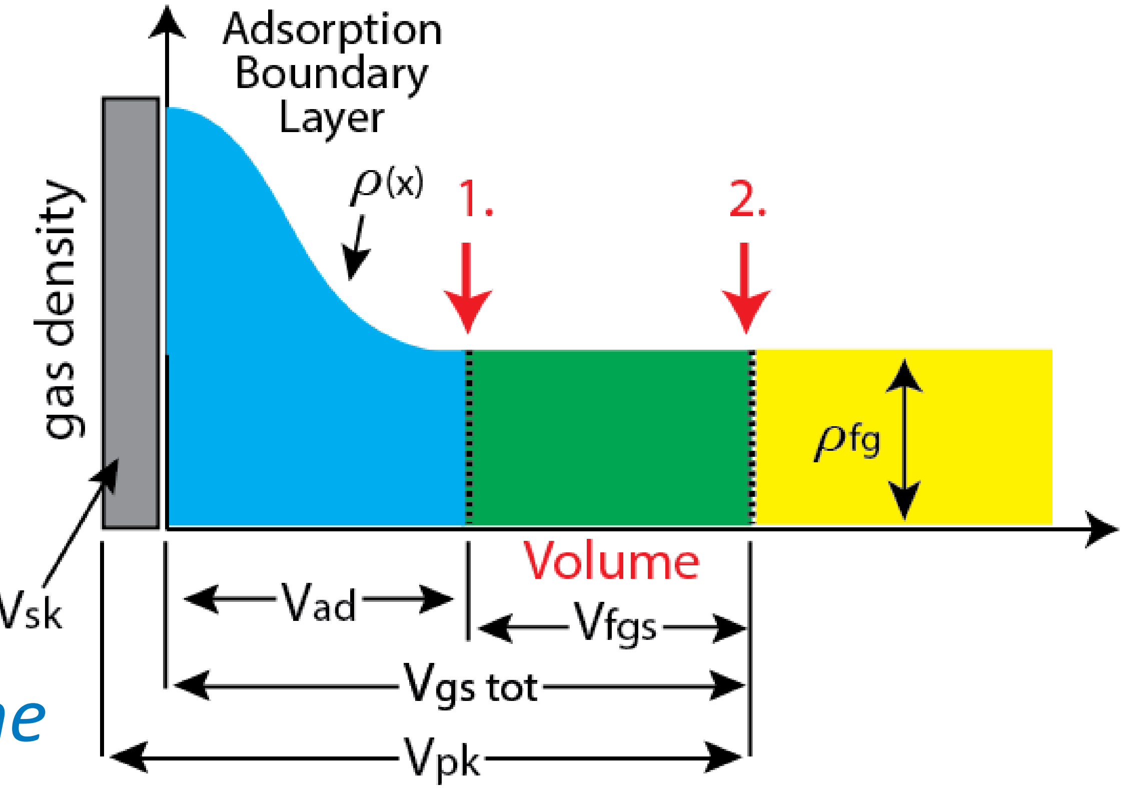
Symbol	Description
Λ_{ec}	Volumetric capacity FOM based on *excess* capacity/crystal volume
Λ_{ep}	Volumetric capacity FOM based on *excess* capacity/packing volume
Λ_{nm}	Volumetric capacity FOM based on *net* capacity/empty vessel volume
Λ_{np}	Volumetric capacity FOM based on *net* capacity/ packing volume
Λ_{tc}	Volumetric capacity FOM based on *total* crystal capacity/crystal volume
Λ_{tp}	Volumetric capacity FOM based on *total* capacity/packing volume
Λ_{ts}	Volumetric capacity FOM based on *total* capacity/total system volume

Definitions, measurement protocols, analysis procedures and reporting recommendations are given in the report.

How To Make Total Capacity Well-Defined?

Two Issues:

1. The boundary between adsorption volume and free-gas region is not known empirically
2. Must define range that the free-gas region extends *for the sample*



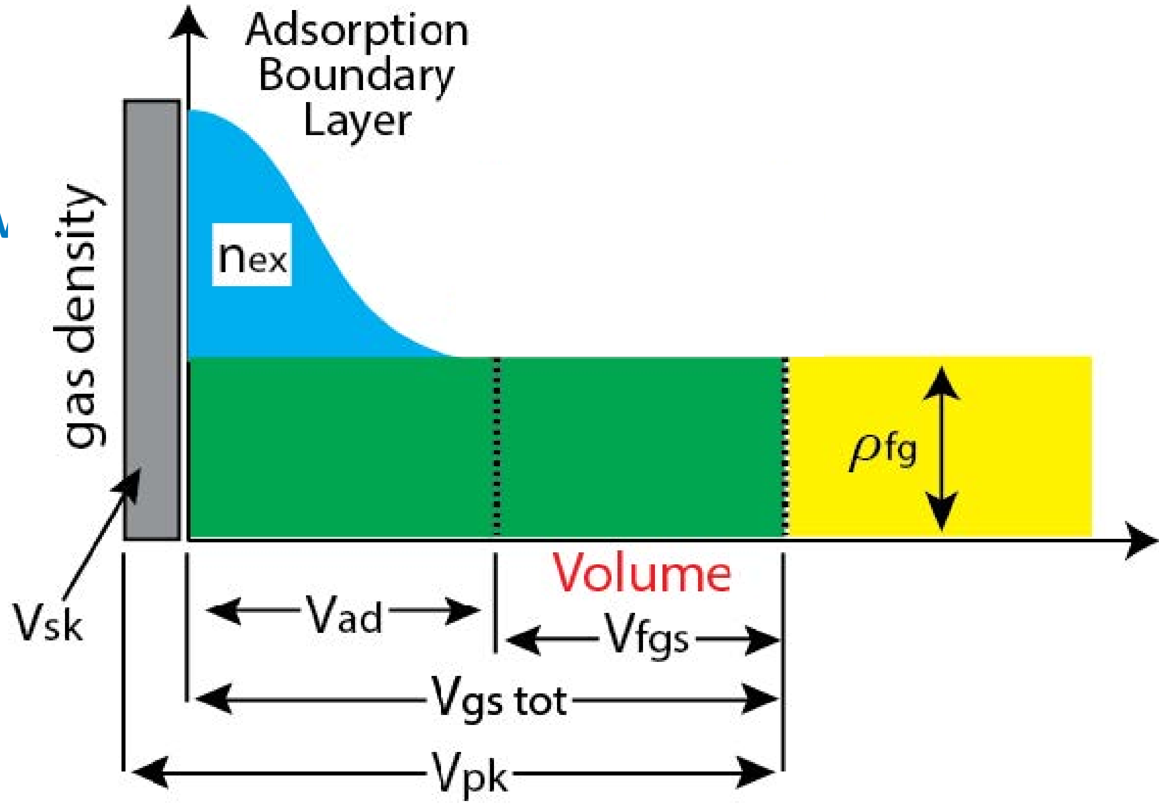
Definition for total capacity

$$n_{tot} = \iiint_{V_{ad}} \rho_g(\vec{x})\, dV + \iiint_{V_{fgs}} \rho_{fg}\, dV$$

Total Capacity Can Be Well-Defined

<u>**Resolution:**</u>

- Re-cast calculation into excess and 'free' gas; now free-gas volume is defined
- Use packing volume as external boundary for sample's free gas
- No possibility of double-counting using this approach



Mathematically equivalent total capacity

$$n_{tot} = n_{ex} + \rho_{fg} V_{gs\,tot}$$

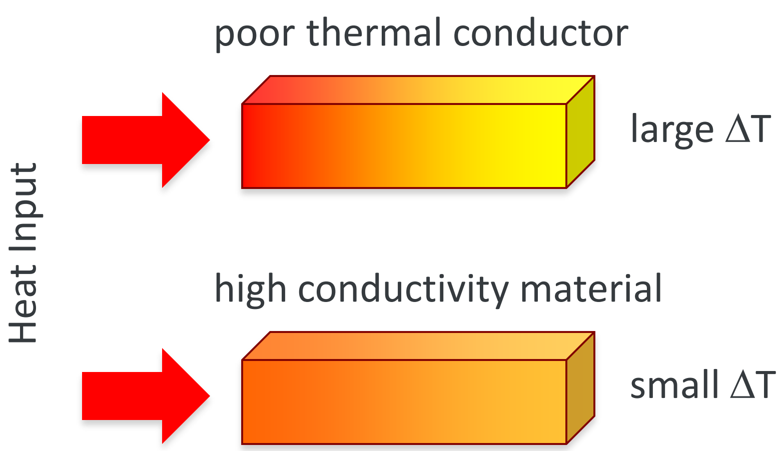
Remaining Challenges and Barriers: Volumetric Capacity

- There remains a great interest and need to have a well-defined absolute capacity determination, but this is extremely difficult as the adsorption volume cannot readily be determined. There currently is no obvious solution moving forward.
- Even though excess, net, and total capacities can be determined experimentally as shown herein, there is considerable interest in determining these quantities calculationally on theoretical crystalline materials. Issues, such as double counting, have not been addressed in the calculations.

Relevance: Thermal Conductivity Measurement & Validation

DOE Objective:

Thermal conductivity measurements for hydrogen-storage materials must be based on valid and accurate results and be conducted under relevant operating conditions to ensure proper identification of promising materials for DOE support and provide engineering data for system design.



Project Goal:

- Develop thermal conductivity measurements for hydrogen storage materials from 77K to 400K, and at pressures up to 150 bar.
  - -Establish methodology for characterizing materials with different form factors.
  - -Validate measurement technique over entire temperature and pressure range.
- Assist materials-research groups to characterize and validate their thermal conductivity measurements.
  - -Measure external samples at NREL to supplement the source group's measurement capabilities.
  - -Validate extraordinary properties claims for novel hydrogen storage materials.

Relevance: Importance of Thermal Conductivity

- **The thermal conductivity of the hydrogen storage material impacts the design of heat exchangers for temperature control.**
  - Low thermal conductivity materials require additives, such as graphite, and/or macroscopic heat-transfer enhancing structures such as fins in the container.
- **The thermal conductivity of the hydrogen storage materials depends on temperature and H_2 gas pressure.**
  - Accurate predictions of material performance require thermal conductivity measurements at the expected operating conditions.
- **A thermal conductivity apparatus that can measure materials over the desired temperature and pressure range is not commercially available and requires customization.**

Approach: Select a measurement technique

Method	Material types	Direct Conductivity Measurement?	Additional Considerations
Steady-state techniques	Solids, powders	Yes	Long equilibration times.
Double-Sided Transient Plane Source (TPS)	Solids, liquids, powders	Yes	Requires 2 identical samples.
Modified Transient Plane Source	Solids, liquids, powders	No	
Single-Sided Transient Plane Source (TPS)	Solids, liquids, powders	Yes	Requires additional validation.
Transient Hot Wire	Solids, liquids, powders	Yes	Requires sample to fully surround wire with good thermal contact.
Optical Flash	Opaque solids	No (standard configuration) Yes (with proper coating and calibration)	Requires optical access in the pressure vessel, porous materials are problematic.

Both single- and double-sided TPS allow for measurements of powders and pucks and can be customized for the temperatures and pressures of interest.

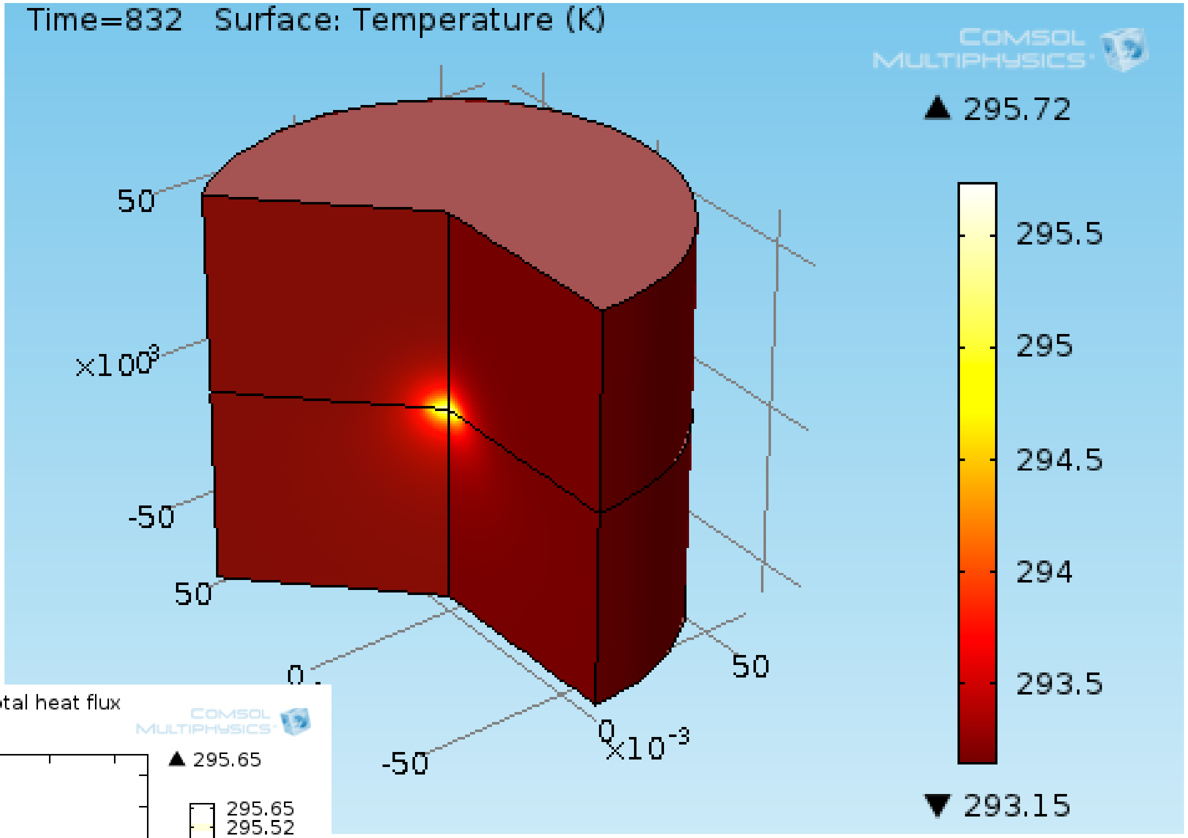
- Single-sided measurement allows for smaller sample volumes.
- Double-sided measurement allows for potentially higher accuracy.

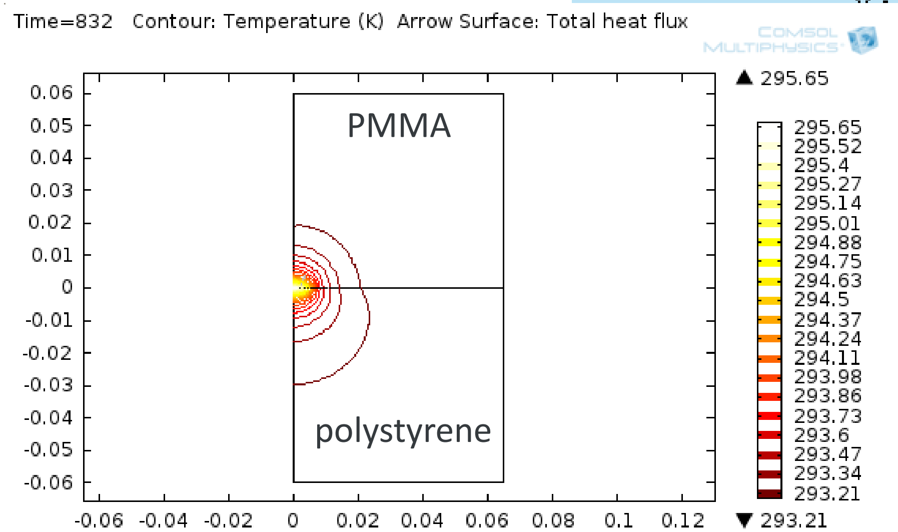
Approach: Design a modular apparatus

- **Model transient temperature profile in single-sided measurement.**
  - No mathematical solutions for this configuration exist in the literature.
  - COMSOL modeling software allows numerical solutions and determination of the functional dependencies for the thermophysical properties of the modeled sample.
- **Design measurement modules.**
  - Design plug-and-play sensor/sample holder units to allow for facile switching between measurement technique and sample form factor.
- **Design system to span temperature range (77K to 400K) and pressure range (0 to 150 bar).**
  - Customize a commercial ***cryostat*** to enable pressurized measurements.
  - Customize a commercial ***pressure vessel*** for electrical measurements.
- **Build and validate the apparatus.**

Accomplishments: Thermal Modeling

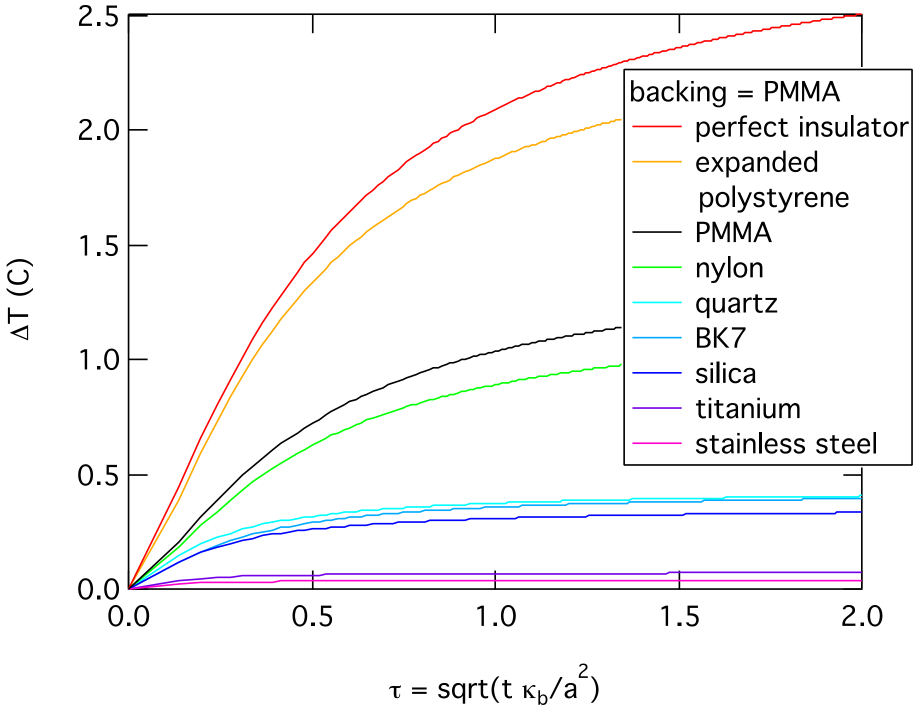
- Heater/sensor is sandwiched between 2 ***different*** materials.
- At t=0, constant power is applied to the heater.
- Resistance change of the sensor reflects temperature change and depends on surrounding materials.
- Magnitude of temperature change depends on both samples.





- **We can model the temperature increase for dissimilar materials.**
- **Modeling is critical as the fitted parameters yield the thermal conductivity & diffusivity.**

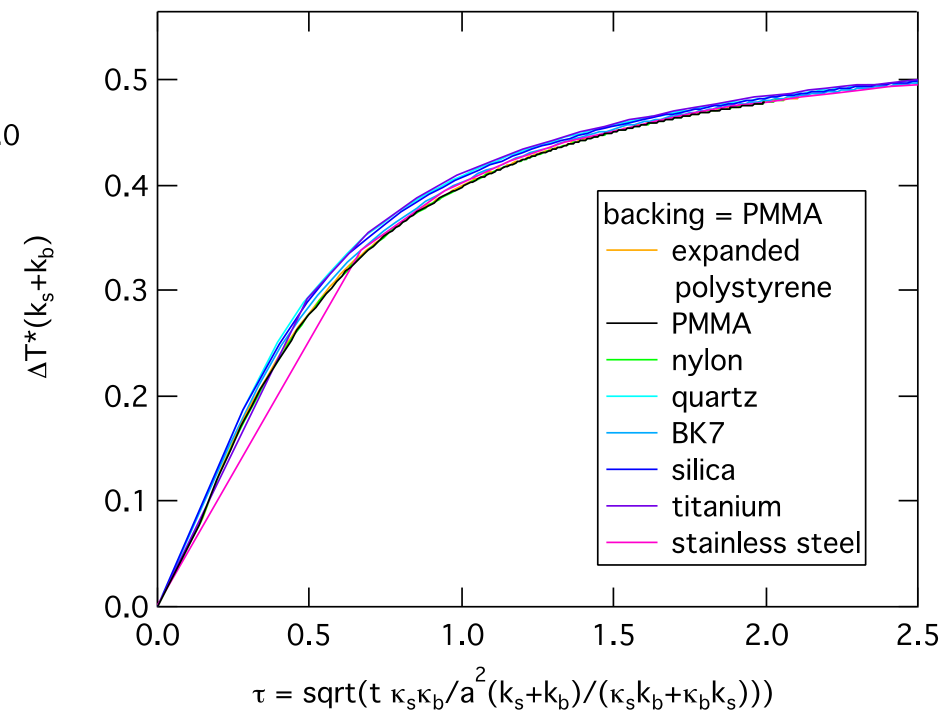
Accomplishments: Thermal Modeling



Proposed Functional Form

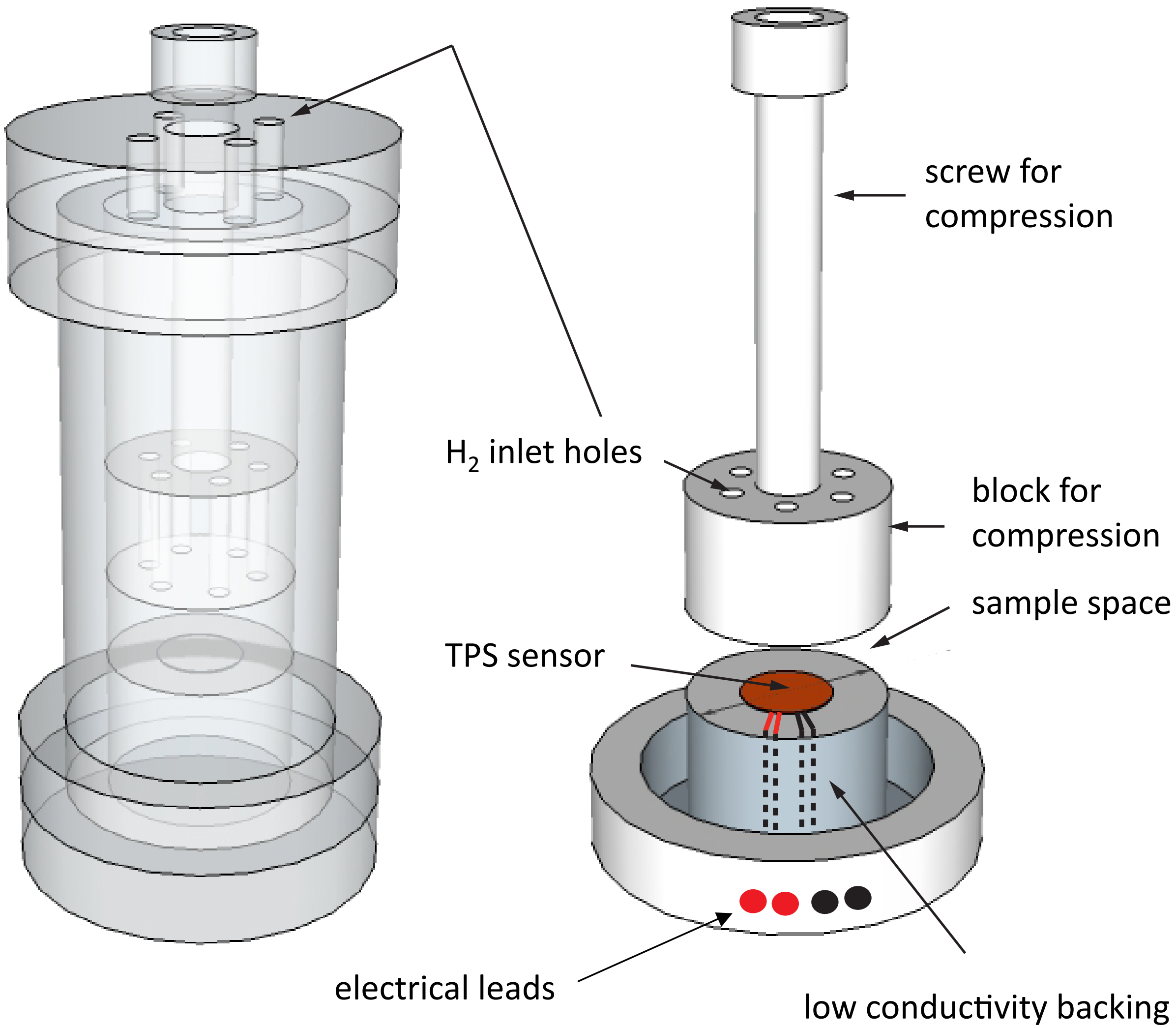
$$\Delta T = \frac{P}{\pi^{3/2} a} \frac{2}{k_b + k_s} D(\tau'')$$

$$\tau'' = \sqrt{\frac{t}{a^2} \kappa_b \kappa_s \left(\frac{k_b + k_s}{\kappa_b k_s + \kappa_s k_b} \right)}$$



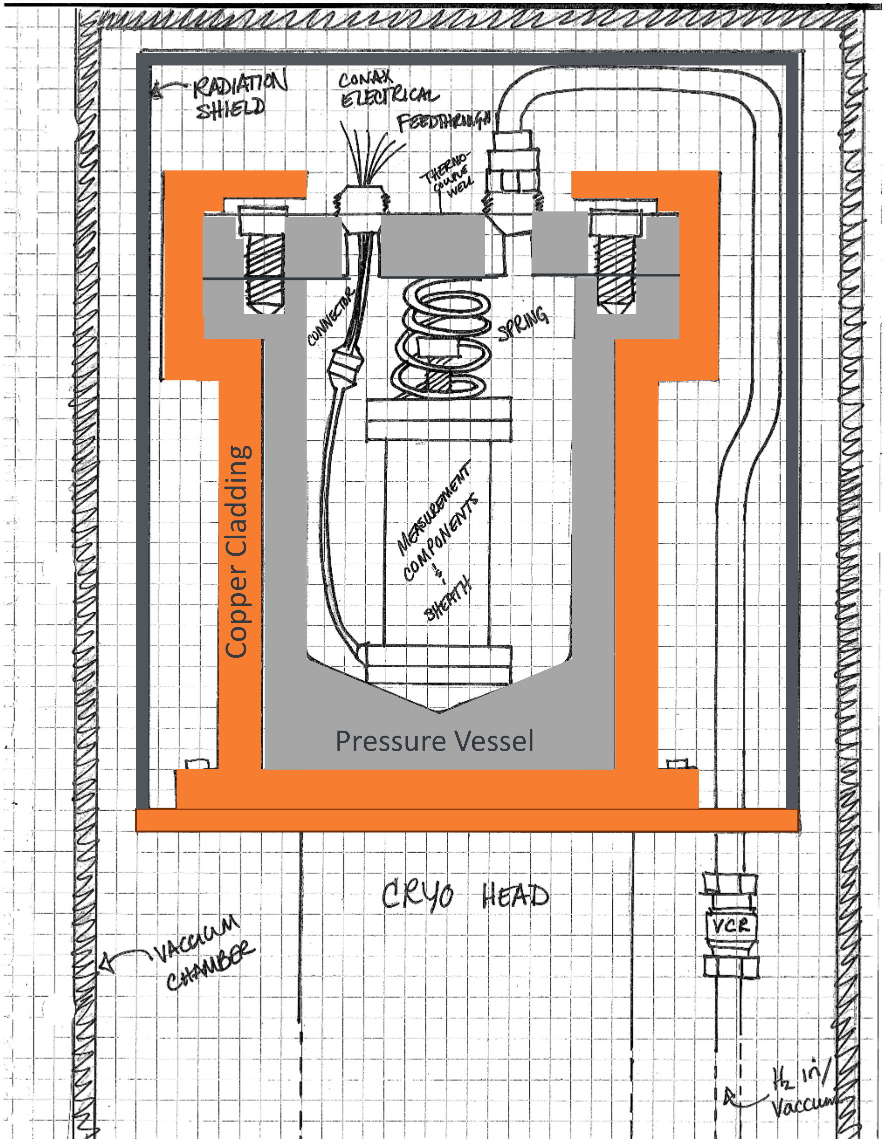
- With the proposed scaling for τ and ΔT, all the simulated material combinations approach a universal curve and allow parameter determination.
- This will require experimental validation.

Accomplishments: Sensor Module Design



- Puck or powder sample placed on top of sensor.
- Block and screw for compression ensure good thermal contact with sensor.
- Hydrogen enters through top.
- Entire module inserted into pressure vessel.

Accomplishments: Design of cryo/pressure system



- TPS module will be inserted into a high-pressure vessel that will be mounted on a cryocooler.
- Additional sensor module designs can be developed to optimize measurements and/or investigate additional geometries/sample types.

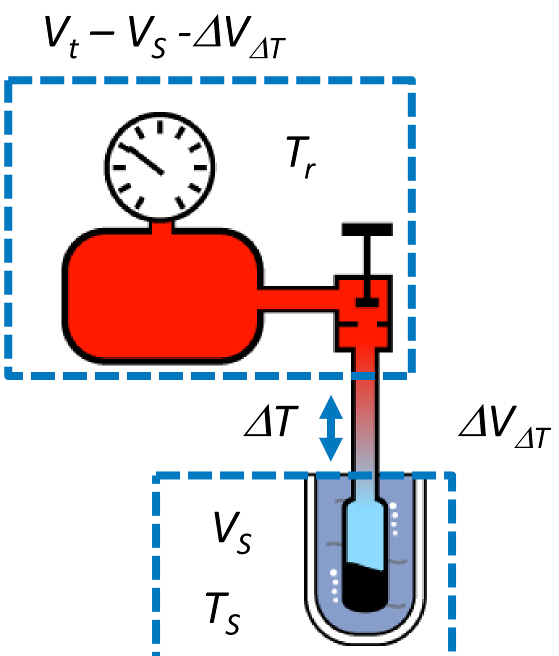
Remaining Challenges and Barriers: Thermal Conductivity

- **The Single-Sided Transient Plane Source models will require experimental validation.**
- **Ensuring hydrogen saturation of samples**
  - The current design allows hydrogen to enter through the top of the module. Dense samples may prevent hydrogen from percolating through the entire sample.
- **Providing uniform compression of powders.**
  - Powder measurements will require a membrane that is permeable to hydrogen, but not to the powder.

Relevance: Measurement Validation & Error Analysis

DOE Objective:

Capacity measurements for hydrogen-storage materials must be based on valid and accurate results to ensure proper identification of promising materials for DOE support.



Manometric (aka Volumetric) System

Project Goal:

- Assist materials-research groups to characterize and validate their samples sorption capacities for hydrogen-storage.
  - -Measure external samples at NREL to compare results with source group's and/or third-party's results.
  - -Discover sources of measurement discrepancies and advise on corrective actions, if needed, for source group.
- Analyze for, identify, and recommend corrective actions for major sources of measurement error in volumetric systems.
  - -Analyze ***realistic*** models for random and systematic errors.
  - -Identify the major error sources that will dominate the measurement.
  - -Recommend improved instrumentation and experimental procedures to minimize such errors.
  - -Analyze materials for chemical reaction by-products.

Accomplishments: Measurement Validation

- **Worked with groups funded by DOE to validate measurements and analyze results.**
  - 2 groups with 3 samples (41 measurements total)

    (Measurements include TPD, PCT, BET etc.)
  - Reported the results to DOE.

    (Data is considered proprietary and cannot be shared.)
- **Collaborated with groups for discussion of error analysis and advisement on protocols to enhance accurate measurements.**
  - 2 groups

Accomplishments: Measurement Validation

- **Presented recommendations for Volume Capacity Conventions to IEA-HIA meeting in January 2015 (meets Milestone).**
- **Manuscript *"Inter-laboratory Comparison of Gravimetric Hydrogen Sorption"* in draft form, invited paper for Applied Physics A. (IEA-HIA)**
- **Co-Authors for overview manuscript for special issues of Applied Physics A. (IEA-HIA)**
- **Report draft "*Recommended Volumetric Capacity Definitions and Protocols for Accurate, Standardized and Unambiguous Metrics for Hydrogen Storage Materials"***
- **Presentation: *"Hydrogen Sorbent Measurement Qualification and Characterization" at the* DOE Materials-Based Hydrogen Storage Summit, Golden, CO January, 2015**

Accomplishments: Milestones

- **Q1 –** Thermal Conductivity Apparatus Design. NREL will submit a draft design to DOE. – 100% completed
- **Q2 –** Present a final report to IEA-HIA Task in Grenoble, France on the new standard necessary for volumetric capacity measurements of hydrogen sorbents.

– 100% completed

- **Q2 –** Thermal conductivity apparatus will be assembled and appropriate readiness verification (RV) and safe work plans (SWP) will be written.

– 90% completed (due to vendor delays, Extended to May 2015)

- **Q3 –** Design and build a thermal conductivity device capable of measurements between 0-100 bar gas overpressure for temperatures from 77K to 358K.

– 50% completed (on target for June 2015)

- **Q4 –** Evaluate, ascertain and validate the gravimetric and volumetric capacity of 2 samples as assigned by DOE. Submit full report to DOE within 30 days of completion of analysis. – 100% completed
- **Q4 –** Perform initial thermal conductivity measurements and work with the Hydrogen Storage Engineering Center of Excellence to determine the validated conductivity of at least 1 adsorbent material. – 10% completed (on target for Sept 2015)

Collaborations

Activities include: technical discussions on equipment and procedures, sample exchange, & data analysis.

- **H2Technology Consulting, USA – Karl Gross**
  - "Best Practices" document, error analysis, & volumetric capacity protocols
- **TAMU, USA – Joe Zhou group**
  - Sample verification
- **UCSD, USA – Seth Cohen group**
  - Sample verification
- **H_2ST^2, USA – Hydrogen Storage Tech Team**
  - Volumetric capacity protocols
- **NIST, Facility for Adsorbent Characterization and Testing (FACT) – ARPA-E Project**
  - Instrumentation & protocol discussion
- **LANL, USA – Troy Semelsberger**
  - Thermal conductivity discussion

Proposed Future Work: Measurement Validation

- **Publish report on volumetric capacity definitions and protocols.**
- **Validate measurements for hydrogen sorption.**
    - Milestone of 2 external samples already met for FY15, but will continue this effort in FY16.
- **Propose an Inter-laboratory Volumetric Capacity Hydrogen Adsorption Study (FY16).**
    - Similar to our previous gravimetric capacity study
- **Develop new capabilities for measuring the hydrogen sorption with increased temperature range (50K – 300K). (FY16)**
    - This involves modification of one of our current PCT systems with a cryocooler.
    - This capability will enable the determination of the isosteric heat of adsorption.

Proposed Future Work: Thermal Conductivity

- **FY15—Build and validate the apparatus.**
  - Assemble all the components including at least one drop-in module, beginning with the single-sided, solid puck module.
  - Measure the thermal conductivity of several standard materials and determine accuracy of the instrument.
  - Validate the measurement of at least one hydrogen storage material.
- **FY16—Assist materials-research groups to characterize and validate their samples.**
  - Measure external samples at NREL.
  - Validate materials properties claims on novel materials.
  - Conduct studies to determine the effects of cycling on the thermal properties of promising hydrogen storage materials.

Summary

- **Protocol Development & Measurement Validation**
  - Report draft *"Recommended Volumetric Capacity Definitions and Protocols for Accurate, Standardized and Unambiguous Metrics for Hydrogen Storage Materials".*
  - Verified measurements on 3 external samples.
  - Recommended improvement to instrumentation and experimental procedures to minimize errors.
- **Thermal Conductivity Measurement**
  - Identified appropriate measurement technique.
  - Designed a system for transient measurements of H_2 storage materials over variable temperatures and pressures.
  - Modeled thermal evolution for single-sided measurements.
- **Collaborations**
  - Interacted with 6 groups on measurement techniques and procedures.
- **Proposed Future Work**
  - Validate thermal conductivity equipment and verify measurement results.
  - Verify capacity measurements on external samples.
  - Publish recommendations for volumetric capacity protocols.

NREL Team

- Dave Bobela – Thermal conductivity hardware
- Tom Gennett – NREL's H_2 Storage Program Lead
- Katie Hurst – H_2 sorption measurements & data analysis
- Michele Olsen – Thermal conductivity project lead
- Philip Parilla – Volumetric capacity protocol & error analysis

Technical Back-Up Slides

Clarifications and Assumptions for Total Capacity Calculation

- **Volume where gas resides in the sample is defined with two measurable volumes:**

$$V_{gs\,tot} = V_{pk} - V_{sk}$$

- **Helium is assumed to be in the free-gas state everywhere when performing calibrations for skeletal volume, V_{sk}.**
- **Packing volume, V_{pk}, can be determined using standard procedures for bulk-volume measurements.**
- **When reporting on total capacity, also report procedures for volume determinations and sample preparation.**

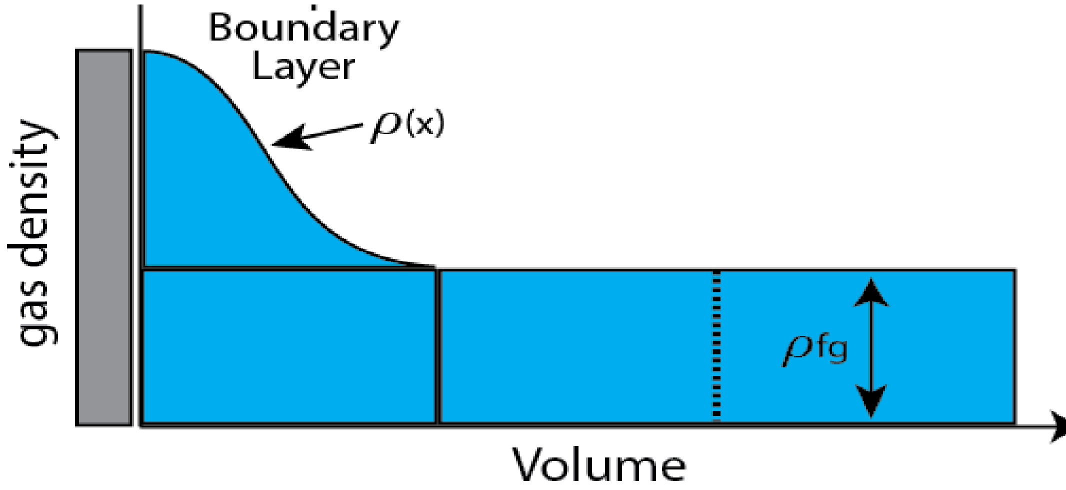
Manometric Adsorption and Defining Volumes

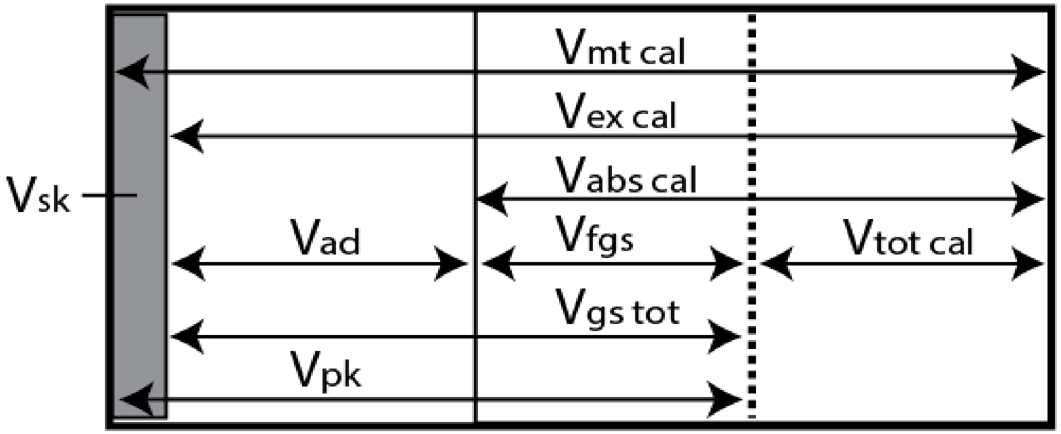
Capacity is determined by subtracting headspace moles from total instrument moles

$$n_{capacity} = n_{totalsystem} - n_{FG}$$

$$n_{FG} = \rho_{FG} V_{cal?}$$ *(FG= Free Gas)*

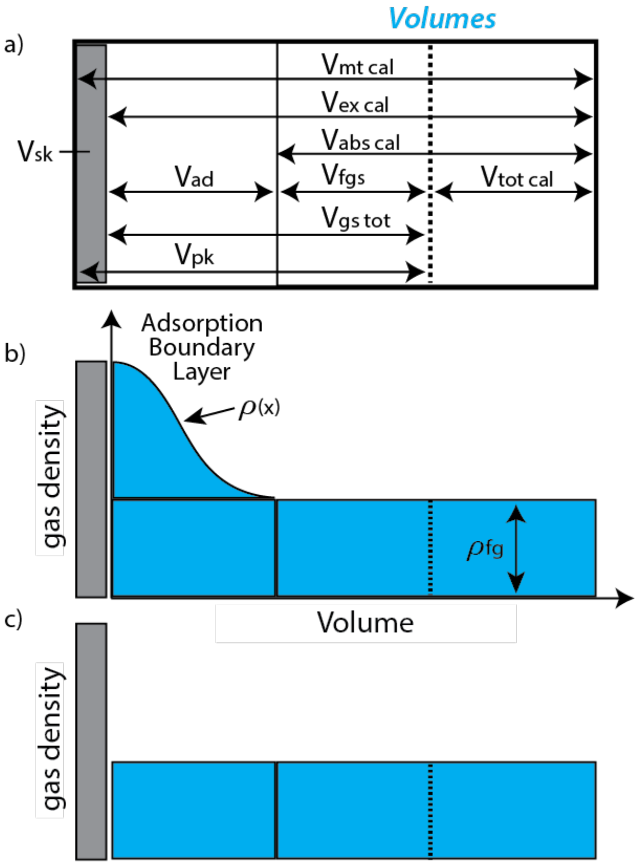
What is the appropriate headspace calibration volume? In principle, we can define headspace constants to determine excess, net, absolute & total capacities.

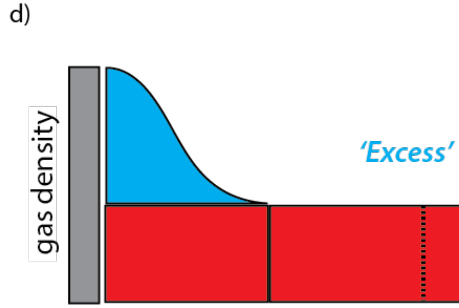




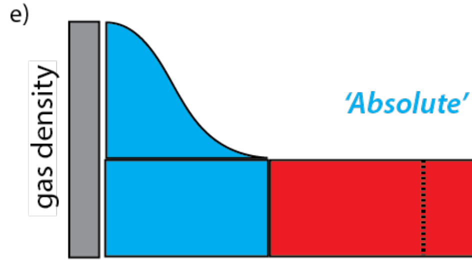
- The volume used for capacity determination must be experimentally measurable.

Manometric Headspace Calibration Equivalencies

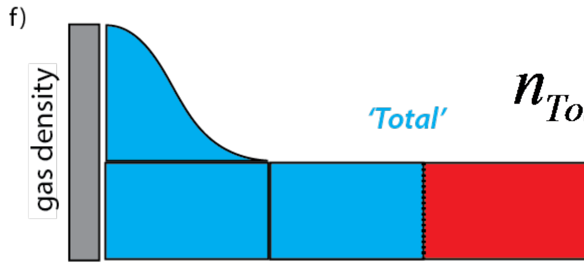




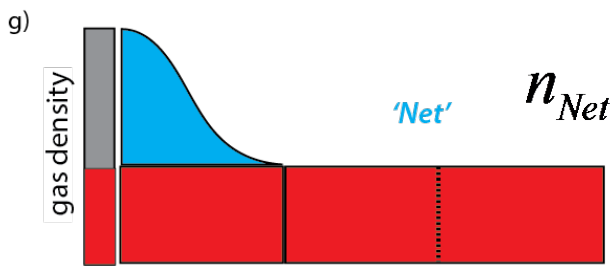
$$n_{Excess} = n_{totalsystem} - \rho_{FG} V_{excal}$$



$$n_{Absolute} = n_{totalsystem} - \rho_{FG} V_{abscal}$$



$$n_{Total} = n_{totalsystem} - \rho_{FG} V_{totcal}$$



$$n_{Net} = n_{totalsystem} - \rho_{FG} V_{mt\ cal}$$

Accomplishments: Lab Infrastructure Upgrades

Before

After

New processed chilled water lines

Space for scroll pumps

Space for cryo compressors

Storage for up to 3 gas cylinders

Additional upgrades:

- 2 New 3 phase, 208V outlets
- 1 New 110V outlet
- New vacuum lines into laboratory
- New pass-through to route cryogenic lines to experimental setup