Hydrogen Sorbent Measurement Qualification and Characterization

2014 U.S. DOE HYDROGEN and FUEL CELLS PROGRAM and VEHICLE TECHNOLOGIES OFFICE ANNUAL MERIT REVIEW and PEER EVALUATION MEETING

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ST014

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Overview

Timeline*

Start: October 2012
End: to be determined
% complete FY 14: ~70%

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

Budget

Funding FY14: $400k
Funding FY13: $300k
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

ORNL & MU, USA– Raina Olsen

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

NIST, USA – Laura Espinal group

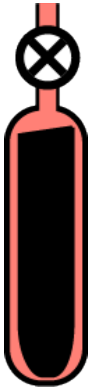
FBK, Italy – M. Testi & L. Crema

Univ. of South Alabama – J. Burress group

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.
- Submit a report that will be disseminated to the scientific community.

Relevance: Importance of Volumetric Capacity

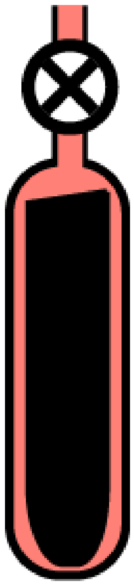
- Volumetric Capacity (VC) is a crucial figure of merit (FOM) to evaluate H_2 storage materials
- Ill-defined VC determinations obfuscate material evaluations and allow overly optimistic reporting
- Need standardized and well-defined VC definitions and protocols to clear up ambiguities
- We propose to explore and clarify VC conventions and protocols to provide guidelines for VC implementations
- We solicited IEA participation to ensure a careful & comprehensive implementation

Approach: Addressing the Issues

- **Conventions**
  - Accounting for hydrogen
  - 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

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

Kg H_2/L

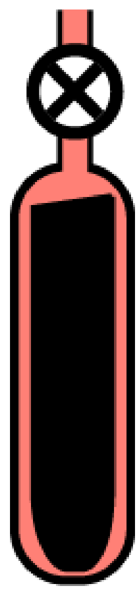


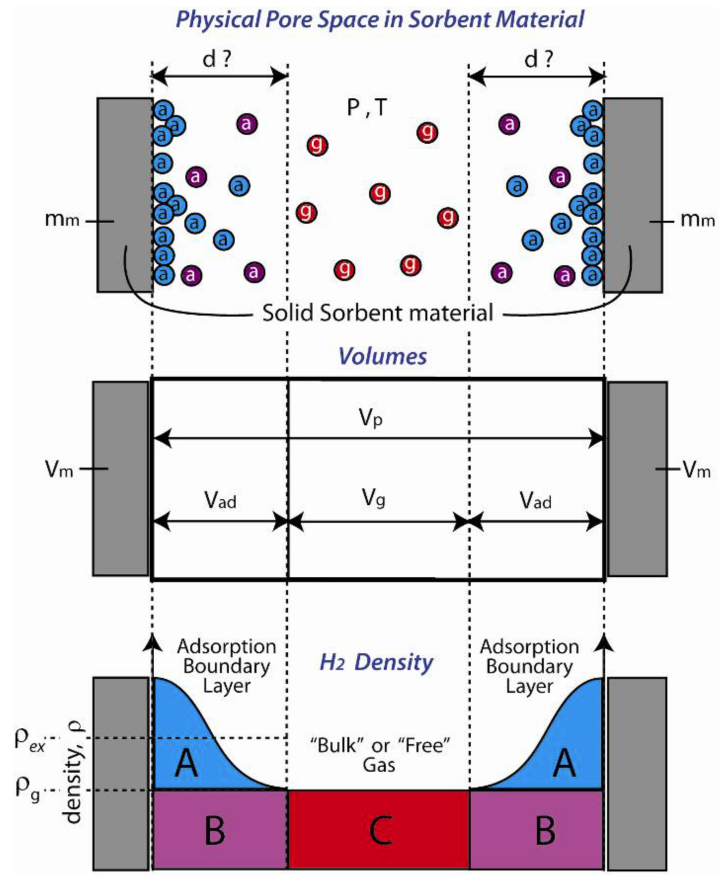
Accounting for the Hydrogen

Different ways to count H_2:
Excess, Absolute, Total

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

No Double-Counting the Hydrogen!!!





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

Adapted from Best Practices, K. Gross

Accounting for the Volumes

There are various types of volumes to consider

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

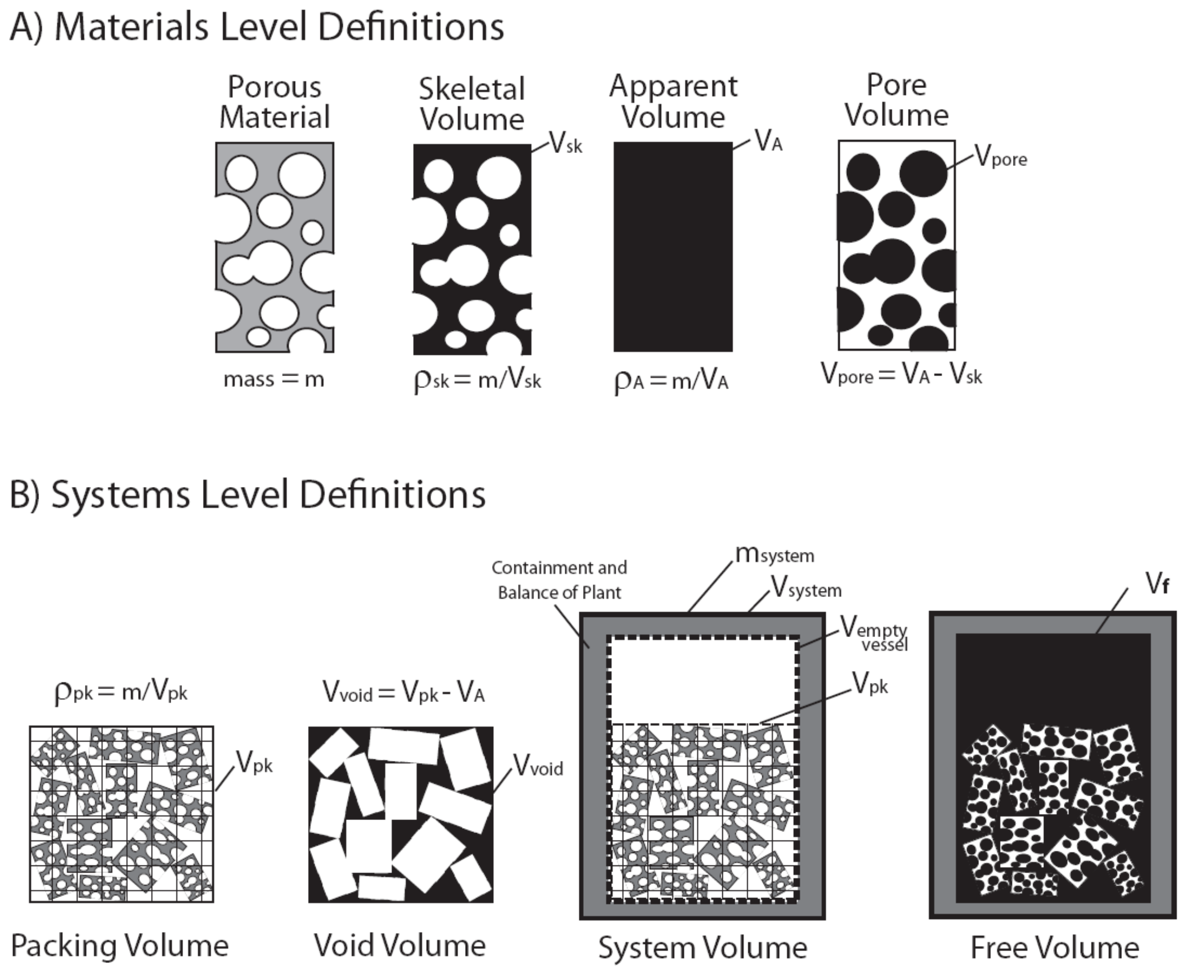


Fig. 84 from Best Practices, K. Gross

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

Approach: Best FOM for a Given Situation

- **Tailor volume capacity convention to match specific goals**
  - Toward material evaluation, comparison and material optimization
    - Skeletal volume, ability for compaction, material expansion
  - Toward engineering considerations and system optimization
    - Balance of plant volume, heat transfer, insulation, material expansion
  - There exists overlap between the two
    - Anticipate overall requirements
    - Develop & disseminate engineering targets

Accomplishments: Volume Capacity Conventions

- **Material Centric**
  - Excess Capacity/Bulk Volume
    - Maximize excess cap., minimize skeletal volume, maximize compaction
  - Total Capacity/Bulk volume
    - Maximize total cap., minimize skeletal volume, maximize compaction
- **Engineering Centric**
  - Total Capacity/System volume
    - Temperature range, thermal conductivity, total energy
  - Engineering Capacity/Empty tank volume
    - Better off with a compressed gas only?

(See technical-backup slides for more conventions)

Accomplishments: Volume Capacity Conventions

RECOMMENDATIONS

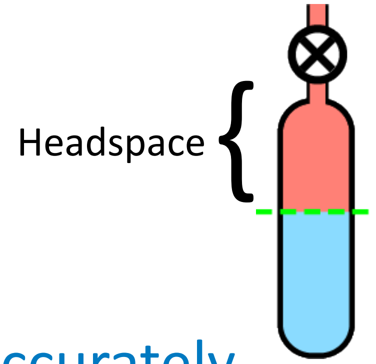
- **Material Centric**
  - Total Capacity/Bulk Volume
    - Maximize total cap., minimize skeletal volume, maximize compaction
- **Engineering Centric**
  - Total Capacity/System Volume
    - Temperature range, thermal conductivity, total energy
- **Important Considerations for Reporting**
    - List assumptions
    - Describe measurement methodology and calculations
    - Give values for inputs to the calculation (bulk density, etc.)

Using Sieverts Approach for VC Determination

Sieverts approach is perfect for determining Total Capacity

- Sieverts calculation works by subtracting moles in "headspace" (aka dead space, void volume) from total moles
- By defining the headspace properly, you can determine the total capacity directly, i.e.,

$$V_{headspace} = V_{empty} - V_{bulk\,volume\,of\,sample}$$



- Bulk volume (bulk density) of the sample must be accurately known as this can dominate the result
- This will determine all the H_2 in the bulk volume (both adsorbed and in pores) and avoids any double-counting of moles – no need to estimate moles in pores independent of excess adsorption – no possibility of double counting

(See technical backup slides for more detail)

Using Gravimetric Approach for VC Determination

- **Gravimetric approach must add the gas moles**
  - Additional moles of the gas phase can be added to excess capacity determination

$$\sum_i m_{i\,H_2} = m_{ex-grav} + \frac{A_{H_2} P \sum_i V_i}{R\,T\,z(P,T)}$$

  - This is similar to the buoyancy correction, i.e., if

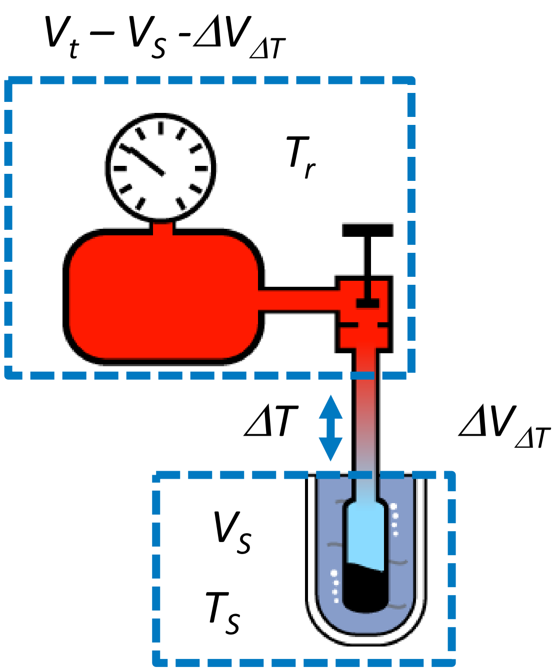
$$V_{buoyancy} = V_{bulk\,volume\,of\,sample}$$

    then the total capacity will be determined.
  - Need excellent estimations for defining volumes and ensuring that they are realistic
    - For porous samples, the gaseous component can dominate
    - Need accurate value for bulk volume (bulk density)
    - Densification may be an issue: no containment vessel to maintain compaction

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

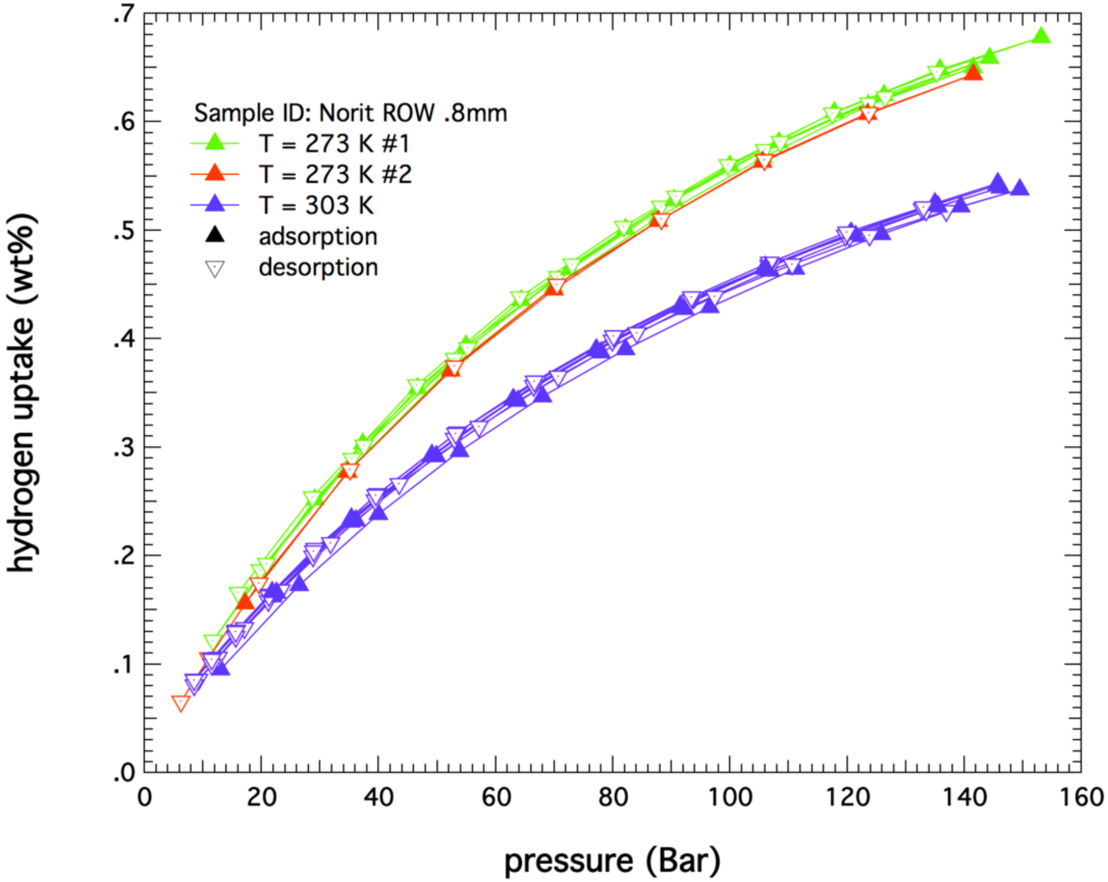
Accomplishments: Measurement Validation

- **Worked with groups funded by DOE to validate measurements and analyze results**
  - 2 groups
  - Reported to DOE the results
    (Data is considered proprietary and cannot be shared)
- **Collaborated with several groups for discussion of error analysis and advisement on protocols to enhance accurate measurements**
  - 4 groups
  - Includes both single-sided and differential Sieverts

Accomplishments: Measurement Validation

- In the process of validating a group's results, the question arose: how much improvement might one see in gravimetric capacity of an activated carbon on going from 303 K to 273 K?
- Measurement was performed on NREL's *de facto* standard material to determine this quantity
- At 140 bar, there is ~22% increase between the two temperatures
- This was consistent with NREL's measurement on the same group's material

Confirming temperature variation of capacity



Accomplishments & Progress: Milestones

- **Q1-** 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.
  - 100% completed
- **Q2-** Evaluate and ascertain the gravimetric capacity of 2 samples as assigned by DOE to validate their performance. Submit full report to DOE within 30 days of completion of analysis.
  - 100% completed
- **Q3-** Establish the figures of merit necessary for determination of volumetric capacity of sorbent materials. Submit a report that will be disseminated to the scientific community at large through either addition to the Best Practices document or other scientific report/publication.
  - 60% completed
- **Q4-** Evaluate and ascertain the gravimetric capacity of an additional sample as assigned by DOE to validate its performance, for an annual total of 3. Submit full report to DOE within 30 days of completion of analysis.
  - Pending assignment by DOE

Collaborations

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

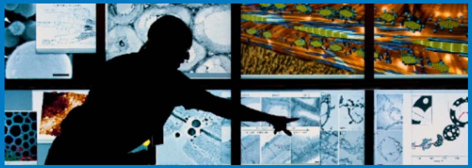
- **H2Technology Consulting, USA – Karl Gross**
  - “Best Practices” document & error analysis
- **ORNL & MU, USA – Raina Olsen**
  - Sample verification
- **NIST, Facility for Adsorbent Characterization and Testing (FACT) – ARPA-E Project**
  - Instrumentation & protocol discussion
- **NIST, USA – Laura Espinal group**
  - Error analysis & protocol discussion
- **Fondazione Bruno Kessler, Italy – M. Testi & L. Crema**
  - Error analysis & protocol discussion for differential manometric system
- **University of South Alabama – Jacob Burress**
  - Sample verification

Proposed Future Work

- **Coordinate with new projects and DOE to ascertain new measurement needs and improve NREL's capabilities to meet those needs**
  - Interface with new FOA projects
  - Help to validate the projects' home equipment
  - Validate sample measurements as needed
- **Continue efforts to measure external samples, assist others in improving measurement procedures, publish error analysis and recommended protocols**
  - Publish recommendations for volumetric capacity protocols
  - Perform analysis for differential manometric system and publish results

Summary

- **Relevance: Protocol Development & Measurement Validation**
  - There is a need for uniform volumetric capacity protocols
  - Implement proper measurement techniques and procedures
- **Approach**
  - Investigate several volumetric capacity conventions
  - Verify measurements on external samples
  - Identify, implement and disseminate corrective measures for sources of error in volumetric systems
- **Accomplishments & Progress**
  - Proposed several volumetric capacity conventions and made recommendations
  - Verified measurements and investigated discrepancies
  - Developed realistic models, identified major sources of errors, disseminated improvement through talks and publications
- **Collaborations**
  - Interacted with 6 groups on measurement techniques and procedures
- **Proposed Future Work**
  - Work with new projects to help validate equipment and verify measurement results



Technical Back-Up Slides

Volumetric Capacity Conventions

Considerations for Volumetric Capacity FOMs:

- So what is the best FOM? Should be tailored to match the specific goals of the project.
- **Material evaluation:**
  - Hydrogen capacity
  - Minimize skeletal volume
  - Compaction without degradation
- **Engineering considerations and system optimization:**
  - Minimize BOP volume
  - Maximize thermal conductivity
  - Minimize insulation
  - Maximize material properties as above

Listing of Possible FOMs:

- **Total Capacity/Bulk Volume:**
  - Includes all the hydrogen in the pores and adsorbed on the surface
  - Bulk volume of the sample is used as the volume with no subtraction of the skeletal volume.
  - **This FOM is recommended as the best definition for materials development**
- **Excess Capacity/Bulk Volume:**
  - Includes only the Gibbsian excess hydrogen adsorbed on the surface.
  - Bulk volume of the sample is used as the volume with no subtraction of the skeletal volume.

Volumetric Capacity Conventions (cont.)

- **<u>Excess Capacity/(Bulk Volume minus Skeletal Volume):</u>**
  - Includes only the Gibbsian excess hydrogen adsorbed on the surface
  - Volume used is the bulk volume minus the skeletal volume.

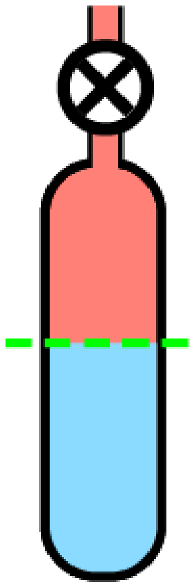
- **<u>Total Capacity/System Volume:</u>**
  - This engineering-centric FOM includes all the hydrogen in the pores and adsorbed on the surface.
  - System volume includes the entire volume of materials, tanks, insulation and balance of plant.
  - **We believe that this FOM is the best definition for system development.**

- **<u>Engineering Capacity/Empty-Tank Volume:</u>**
  - This engineering-centric FOM includes all the hydrogen in the pores, adsorbed on the surface and in the free space of the tank.
  - The empty-tank volume includes the volume of the empty tank and most likely up to and including the isolation valve. This FOM directly addresses the question: Is filling the tank with an adsorbent better than just using an empty tank for compressed gas?

- **Definitions:**
- **<u>Bulk Density:</u> Mass of the sample divided by the volume of the sample. There are many techniques to determine bulk density of a particular type of material. It will involve additional specifications on how the sample was prepared, conditioned, and possibly undergoing a process for compaction.**
- **<u>Bulk Volume:</u> Degassed sample mass divided by bulk density.**
- **<u>Engineering Capacity</u>: Excess capacity minus skeletal volume capacity**
- **<u>Skeletal Density:</u> Mass of the sample divided by the volume of the sample where no gas can penetrate. Usually determined by some form of helium pycnometry.**
- **<u>Skeletal Volume Capacity</u>: The number of gas moles that would exist in the volume equal to the skeletal volume at the sample's pressure and temperature**

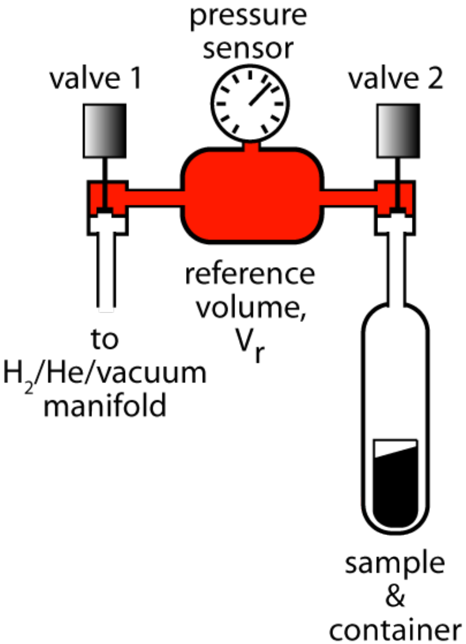
Using Sieverts Approach for VC Determination

- **Sieverts methodology is well-suited for finding total capacity**
  - The null calibration parameter (aka headspace, dead space, void volume) can be used to directly determine Σm_i given ΣV_i and V_{empty}
  - Normally, the null calibration is equivalent to the value $V_{empty} - V_{skeletal}$ and Sieverts yields excess adsorption
  - When the null calibration is $V_{empty} - V_{aribtrary}$, Sieverts yields total hydrogen in $V_{aribtrary}$
  - Choose ΣV_i with $V_{arbitrary}$ to get appropriate Σm_i
  - Example: if $V_{aribtrary} = 0$, Σm_i = engineering capacity
  - The same data set can be used to calculate various VC conventions
  - Assumptions for accurate mole counting:
    - Sample must be contained entirely within $V_{aribtrary}$
    - The volume, $V_{aribtrary}$ must be isothermal, isobaric and contain the adsorbate
    - This can be adapted for non-isothermal measurements where the sample is at an independent temperature from the rest of the instrument

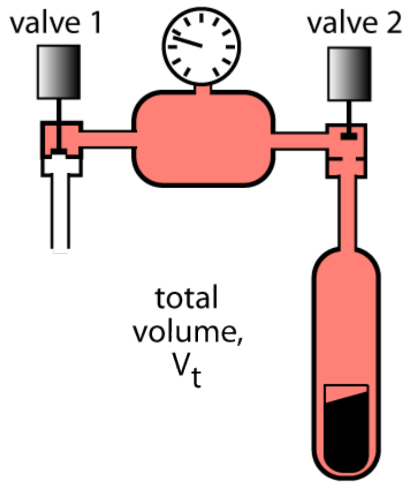


Isothermal Mole-Balance Equations

V_r "state"



V_t "state"



- **"2-state" system**
- **Based on mass balance**
  - **Missing gas = adsorption**
  - **Extra gas = desorption**
- **2 calibration constants**
  - **Null (measuring zero)**
  - **Absolute**

for isothermal system

V_r "state" **V_t "state"**

$$n_{ads_i} = \left(\frac{V_r}{RT}\right)\left[\left(\frac{P_{Ch_i}}{z_{Ch_i}} - \frac{P_{Cl_i}}{z_{Cl_i}}\right) - \gamma\left(\frac{P_{Eq_i}}{z_{Eq_i}} - \frac{P_{Eq_{i-1}}}{z_{Eq_{i-1}}}\right)\right]$$

Moles adsorbed on the i^{th} step

$$\boxed{z_{S_i} = z_{gas}(P_{S_i}, T); \qquad \gamma = V_t / V_r}$$

Non-Isothermal Mole-Balance Equations

- Models have been developed to realistically handle non-isothermal measurements.
- Equation must reflect the volumes at different temperatures and the temperature gradient

$$n_{ads_i} = \frac{1}{R\,T_r}\left[\left(\frac{P_{Chr_i}}{z_{Chr_i}} - \frac{P_{Clr_i}}{z_{Clr_i}}\right)V_r - \left(\frac{P_{E_i}}{z_{Er_i}} - \frac{P_{E_{i-1}}}{z_{Er_{i-1}}}\right)\left(V_t - V_s - \Delta V_{\Delta T}\right)\right]$$

$$- \frac{V_s}{R\,T_s}\left(\frac{P_{E_i}}{z_{Es_i}} - \frac{P_{E_{i-1}}}{z_{Es_{i-1}}}\right) - \frac{\Delta V_{\Delta T}}{R}\left(\frac{P_{E_i}}{\tau_{E_i}} - \frac{P_{E_{i-1}}}{\tau_{E_{i-1}}}\right)$$

$$\boxed{z_{Xk_i} \equiv z\left(P_{X_i}, T_k\right) \quad ; \quad \frac{1}{\tau_{E_i}} \equiv \frac{1}{L}\int_{x=T_r}^{x=T_s} \frac{dx}{T(x)\,z(P_{E_i}, T(x))}}$$