Enhanced Hydrogen Dipole Physisorption

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with DOE Center of Excellence on Carbon-based
Hydrogen Storage Materials

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This presentation does not contain any proprietary or confidential information

Project ID # STP16

Overview

Timeline

- Project start date: October 1, 2004
- Project end date: September 30, 2009

On board hydrogen storage Barriers and Targets

(B) Weight and volume of on board hydrogen storage systems

(N) Low temperatures that physisorption based systems typically need to work in order to store high hydrogen densities.

Budget

- Total project funding
  - DOE share $1M (5 yrs)
  - Contractor share $250k (5 yrs)
- Funding for FY06
  - DOE share $170k
  - Contractor share $42.5k

Partners

Interactions/collaborations:

Jet Propulsion Laboratory (R. C. Bowman, Jr.)

LLNL (T. Baumann, J. Satcher, Jr., J. Herberg)
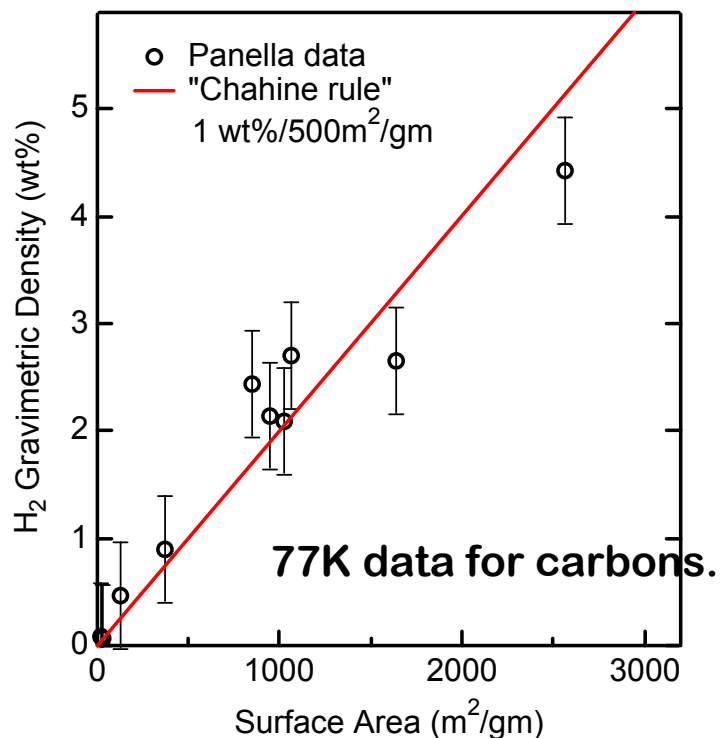
National Renewable Energy Lab. (M. Heben)

CNRS, Grenoble, France (R. Yazami)

NIST (Dan Neumann)

Objectives

- High surface areas will be necessary for physisorbents for non-dissociative H_2 storage. Materials such as activated carbons and carbon aerogels and metal organic frameworks have proven to be effective, if not optimized, candidate materials as they presently work best at 77K temperature and pressures of 30 to 40 bar.

- Further enhancement of surface area needs to be accomplished in order to improve gravimetric density (from our work, presently at 5.4wt% at 77K for a 2447m^2/gm surface area activated carbon).

- Tailoring pore size needs to be addressed to maximize volumetric density (presently ~38gm/liter at 77K). Optimal pore size should be ~1.1 nm in order to maximize volumetric density.

- Sorption enthalpies beyond the 4 to 8 kJ/mole range typical of current materials needs to be increased so that sorbents can work at ambient temperatures.

Approach:

- Gravimetric density observed to scale with surface area in physisorbents as shown below, in most materials so maximizing surface area in physisorbents a vital criterion for these materials.

- Adsorption/desorption evaluation with volumetric Sieverts apparatus capable of measurements of samples at 77, 87, 195, and 298K temperatures.

  Differential enthalpy of adsorption measurements at zero coverage in order to identify adsorption "heats".

 We have over 10 years experience with volumetric hydrogen sorption measurements.

  Computer controlled unit is 3rd generation Sieverts, built at JPL from unit originally built at Caltech.

Plot legend:
○ Panella data
— "Chahine rule"
1 wt%/500m^2/gm

Y-axis: H$_2$ Gravimetric Density (wt%)
X-axis: Surface Area (m^2/gm)

77K data for carbons.

from "Hydrogen adsorption in different carbon nano-structures," B. Panella, et al, Carbon, 43, 2209, (2005)

# Technical accomplishments: Isotherm dependency analysis

For carbon aerogels synthesized by CbHS partner Lawrence Livermore National Lab., we note that gravimetric density scales with surface area as seen in activated carbons and is shown at the right, where we compare 77K isotherms traces for several surface areas. Below we show the specific surface area dependence and overlay our data with that from the literature.
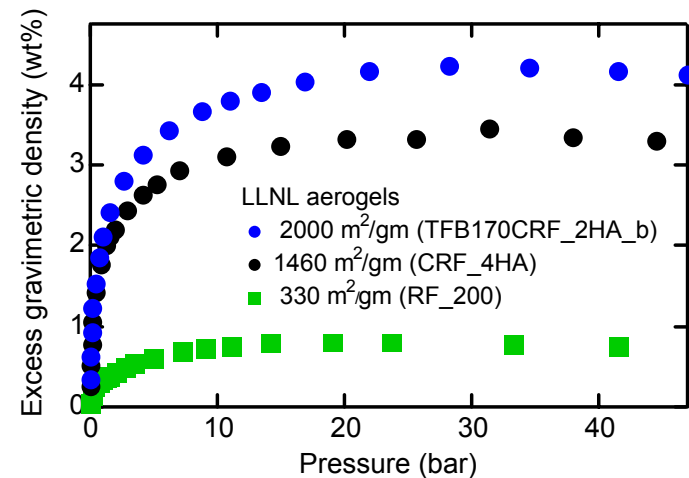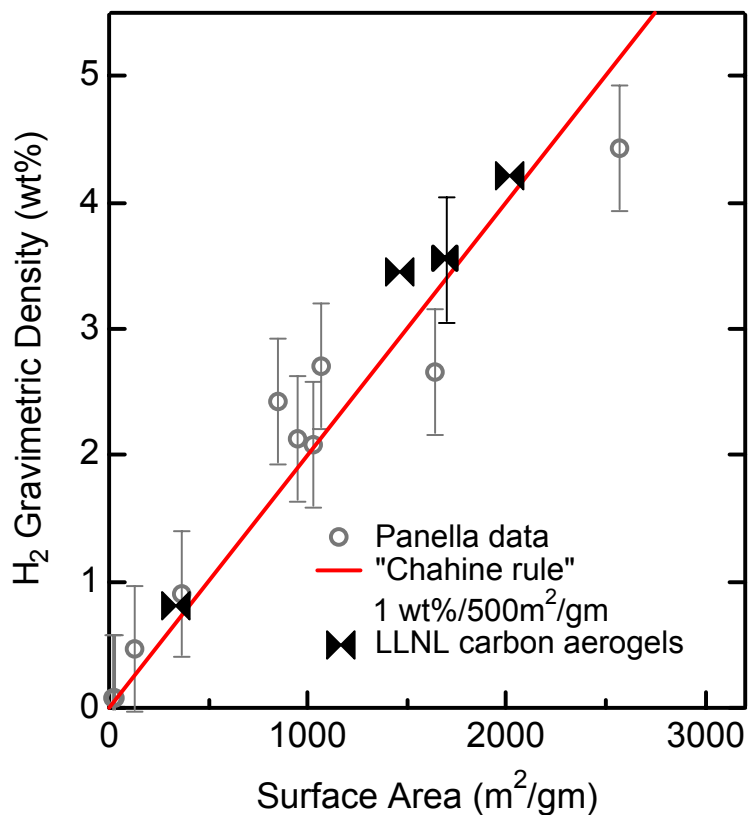
For materials in the 4kJ/mole adsorption range, low temperatures are necessary in order to maximize gravimetric density as shown in our data for a metal organic framework, IRMOF-1 as shown below.
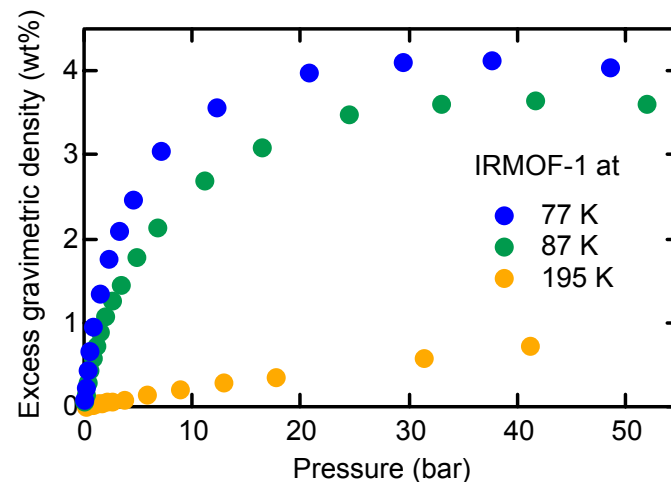
Technical accomplishments: Initial steps at further improving sorption behavior in LLNL aerogels with catalytic additions
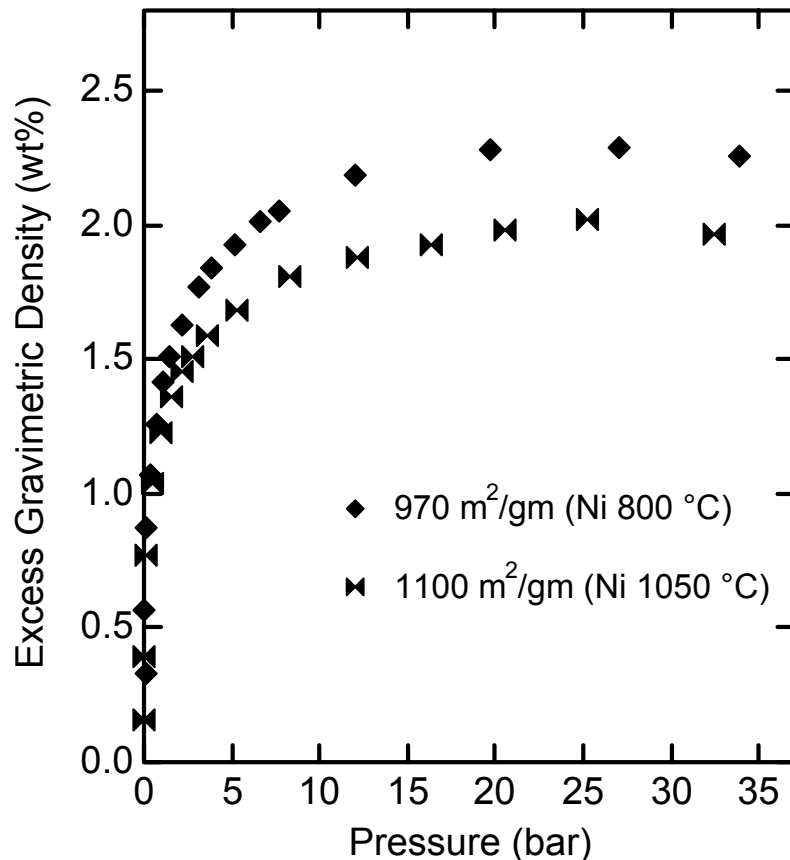
- Catalytic additions have been shown to enhance sorption over that of similar surface area materials.
- Plot at left compares 77K isotherms of lower surface area catalytically active (Ni catalyst has clean surfaces) aerogel with that of a higher surface area non-catalytically active aerogel (Ni catalyst particles are encased in graphitic carbon, rendering them inactive) .
- Enhancement of the catalytically active material seen in the higher sorption isotherm trace.
- Effect related to work of J. Schwarz of Syracuse, "Metal assisted cold storage of hydrogen," U.S. patent 4,716,736.

Technical accomplishments: IRMOF-1 and IRMOF-8 synthesis, isotherms and analysis
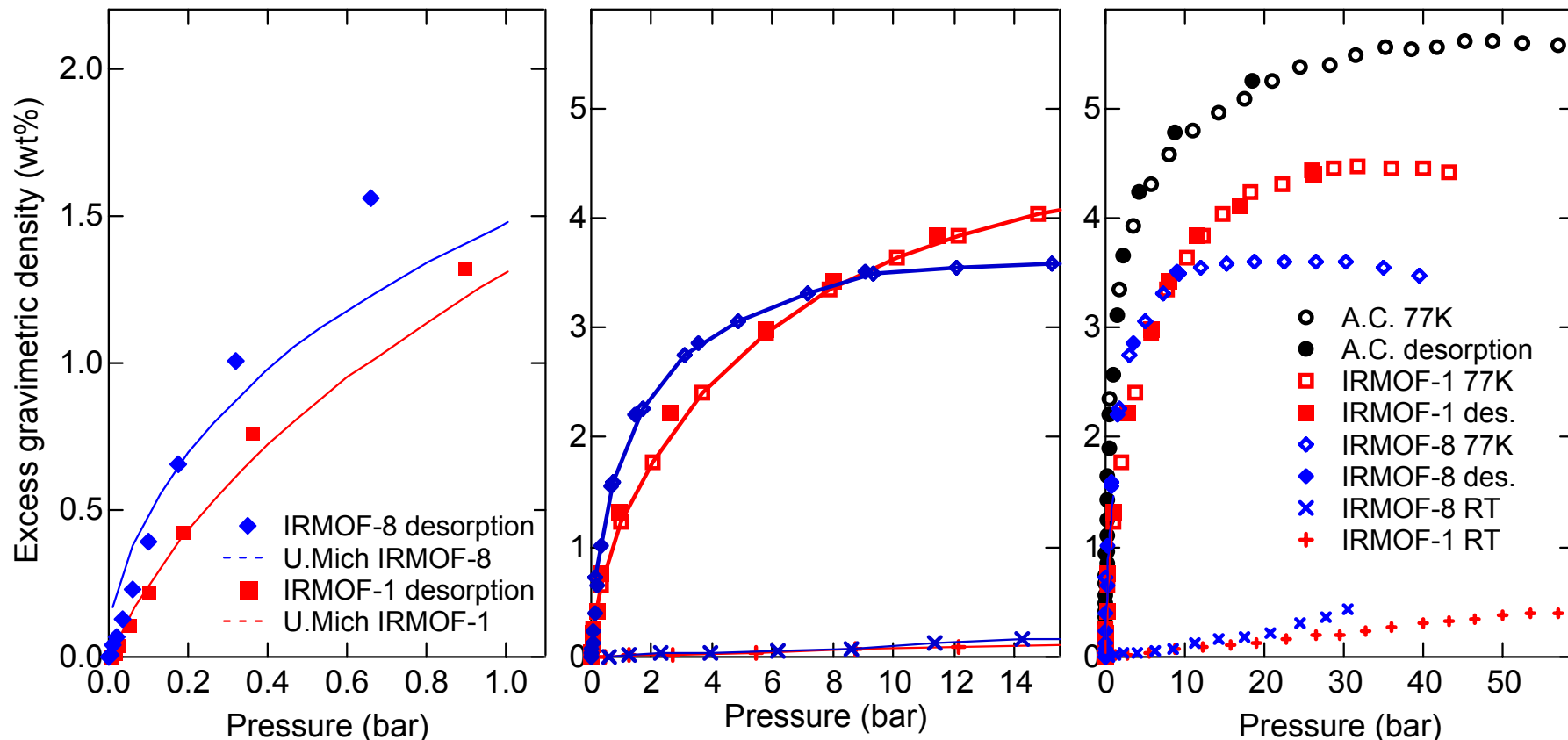

- Our work on IRMOF low pressure data to 1 bar in left plot show that this data range not a predictor of saturation behavior, only an indication of sorption heat (high slope => higher heat, IRMOF-1 ~4kJ/mole, IRMOF-8 ~6kJ/mole).
- Middle plot shows cross-over of sorption behavior at 8 bar pressure.
- Right plot shows saturation behavior of metal organic framework structures compared with high surface area, and tailored pore size activated carbon sample from F. Baker and N. Gallego, Oak Ridge National Lab. IRMOF's show surface area dependence also and these data consistent with a lower surface area measured in IRMOF-8 (1800m^2/gm) vs IRMOF-1 (3100 m^2/gm).

A. Dailly, J. J. Vajo and C. C. Ahn, J. Phys. Chem B, v110, p1099, (2006)

# Accomplishments: Volumetric activated carbon (AC) analysis at 77K

For a volumetric analysis we need to take into account a) the volume of sorbent (as determined by the skeletal density), b) the volume of the adsorbed gas and c) the volume remaining given the overall density of the material. Assume we can start with a high surface area AC with a ~0.6 gm/cc overall density, that has a 2.1 gm/cc skeletal density, in a 1000cc volume.
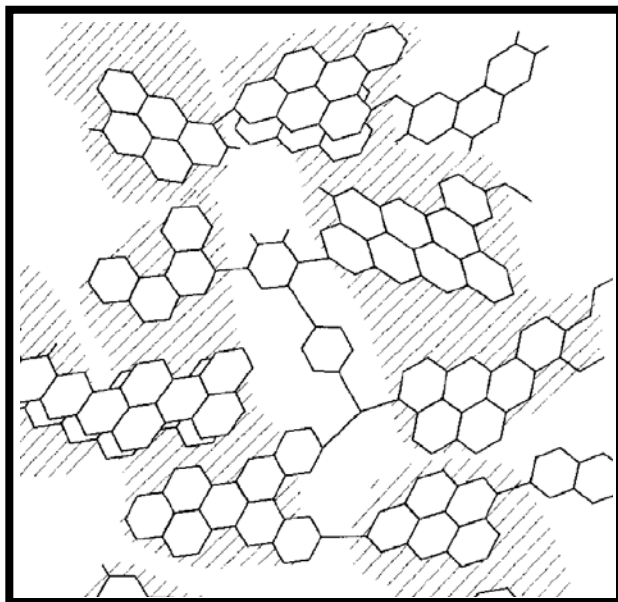
At 0.6 gm/cc => 600 gm of AC and 600gm/2.1gm/cc or 285 cc volume occupied by activated carbon sorbent only.
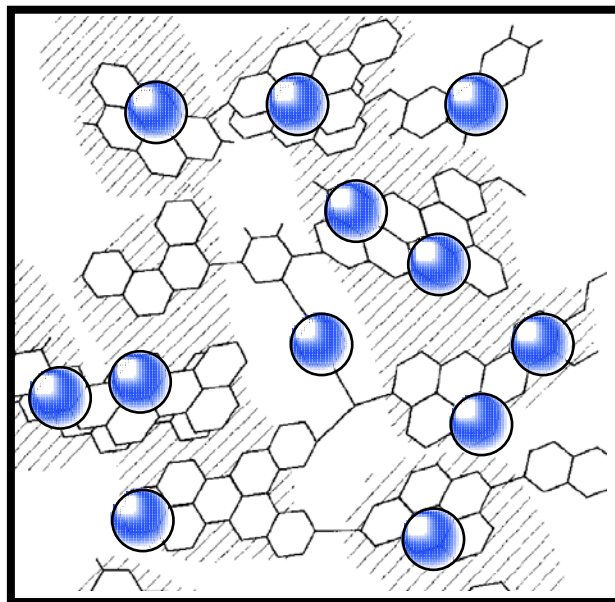
Assuming a 5.5wt% hydrogen storage value, ~35gm H_2 adsorbed 1000 cc volume. If density of adsorbed layer similar to LH_2 density, then ~500 cc is occupied by adsorbed H_2 gas and ~215 cc is left as "free" volume.
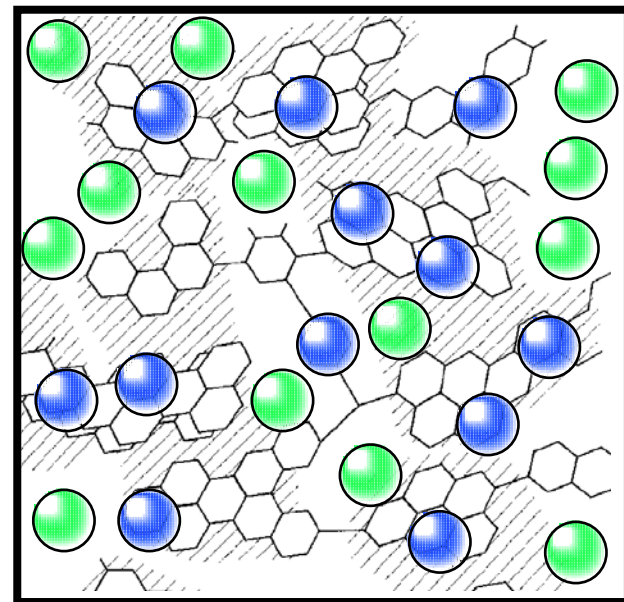
Apply gas law to remaining 215 cc void to estimate total storage yields a total density of 38gm/liter including adsorbed and gas law contributions (analysis in background slide).

Planned Work for FY2006/FY2007

- Continued collaboration with LLNL on aerogel analysis including:
  - ☐ Boron incorporation into aerogel structure to improve adsorption enthalpies as a means of using physisorbents at ambient temps.
  - ☐ Incorporation of catalysts in higher surface area aerogels to improve gravimetric densities over the 5.4wt% presently achievable.
  - ☐ Synthesis of MIL (Material Institut Lavoisier) high surface area structures to improve gravimetric densities.
- Optimization of pore size/volume in order to maximize volumetric density. An ideal graphitic structure with a 1.1 nm pore size can accommodate as much as 7.7 wt% gravimetric and, from 44 to 58 gm/liter volumetric density.
- Continuation of evaluation of thermodynamic properties (isosteric enthalpy of adsorption and differential enthalpy of adsorption at zero coverage).

Project Summary

- Relevance: Physiorbents for non-dissociative hydrogen storage offers higher storage densities than compressed gas storage.

- Approach: Synthesis of high surface area physisorbents (in order to achieve gravimetric densities of 7.7wt%) with tailored pore size (to reach volumetric densities of 58 gm/liter) and high adsorption enthalpies (ambient temperature operation) our key goal.

- Technical accomplishments and progress: Study of large range of carbon based materials including activated carbon, aerogels and metal organic frameworks to show that gravimetric densities scale with surface area and that these materials have sorption enthalpies of 4-8 kJ/mole.

- Collaborations: JPL, LLNL, ORNL, NREL, NIST, CNRS (France)

Project Summary

On-Board Hydrogen Storage System Targets (**Data is based on material only, not system value)				
Storage Parameter	**Units**	**2010 System Target**	**FY06 materials****	
Specific Energy	kWh/kg (wt. % H2)	2.0 (6 wt.%)	1.91 5.4 wt% at 77K	
Volumetric Energy Capacity	kWh/L	1.5	1.28	

Background: Volumetric density analysis
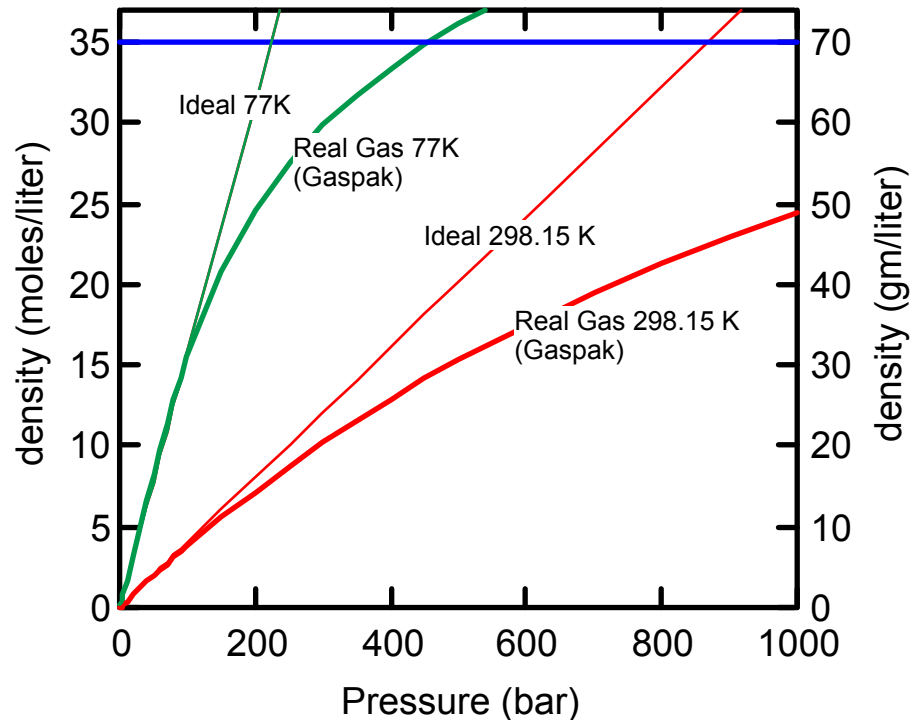
Real vs ideal gas behavior understanding necessary in determining volumetric behavior. Equations of state determined from "Gaspak" software updated from hydrogen properties from NBS Technical Monograph 168, February 1981, (R. D. McCarty, J. Hord and H. M. Roder). Equation of state valid from triple point to 5000 K, pressures to 1200 bar.
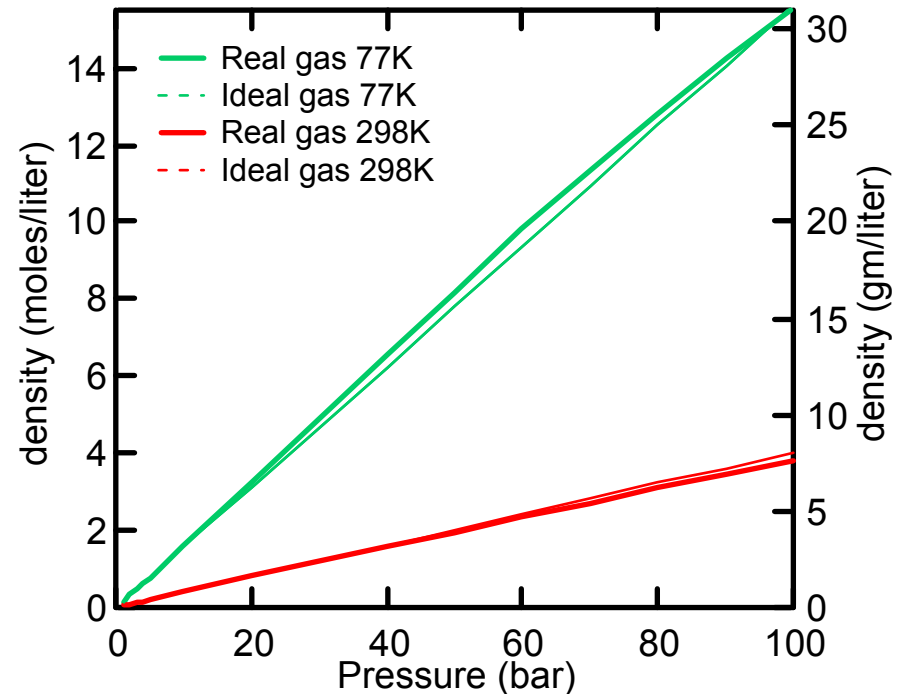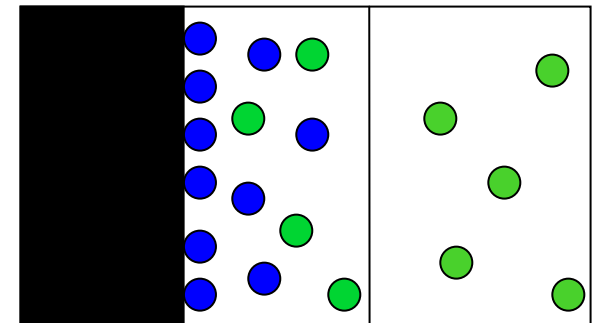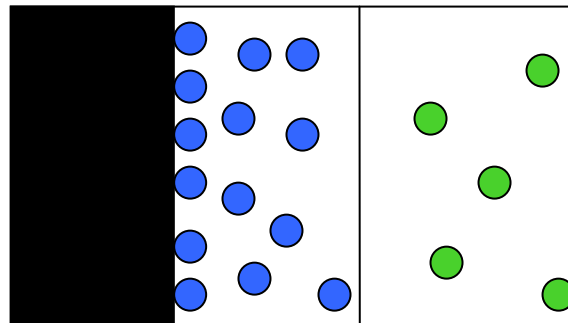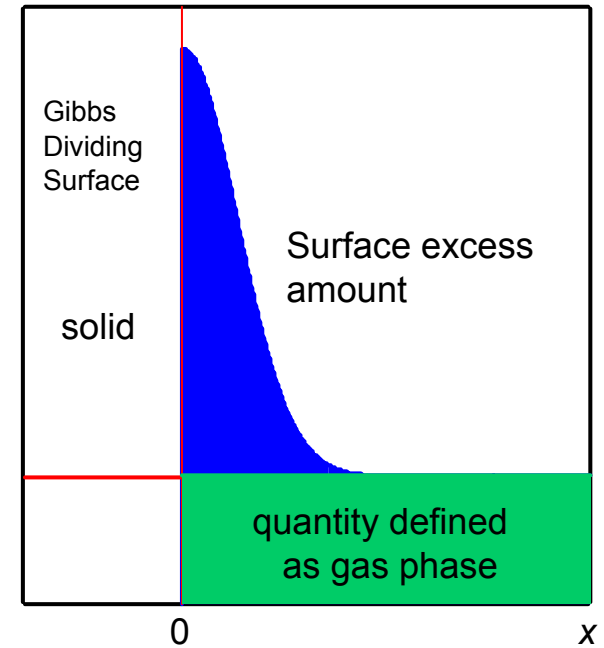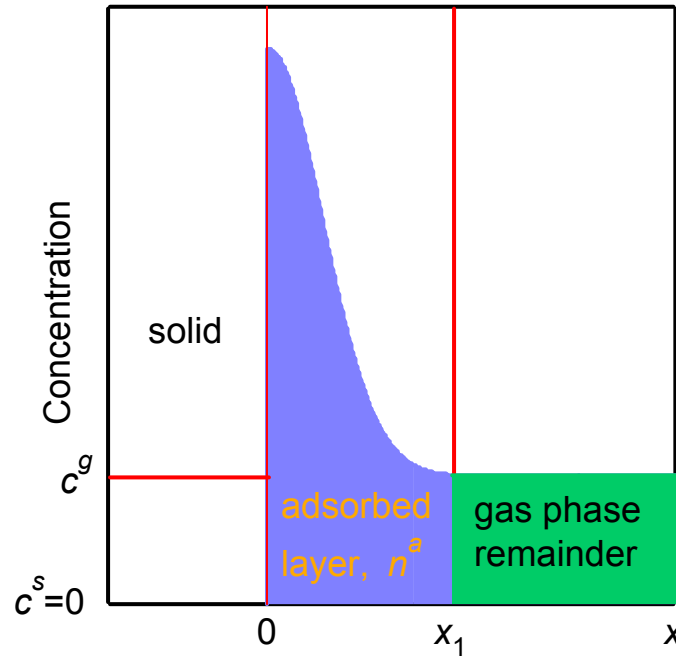
At pressures to 100 bar, real and ideal gas behavior similar for both 77K and RT

Background: Volumetric density analysis, surface excess adsorption assumptions

- Adsorbed gas concentration difficult to quantify. Data typically presented as "surface excess quantity" and given thermodynamic meaning by use of Gibbs dividing surface.
- Need to make assumptions regarding the concentration profile of surface excess amount in order to know volume taken up by the adsorbed layer.

- If we assume that the adsorbed surface density comparable to LH2 density, then we can apply gas law to our analysis.

Concentration

c^g

$c^s = 0$

solid

adsorbed layer, n^a

gas phase remainder

0   x_1 x

Gibbs Dividing Surface

solid

Surface excess amount

quantity defined as gas phase

0   x

Background: Gas law contribution analysis to total sorbtion based on available volume

Assuming a 215 cc remaining volume available with which to apply the gas law:

where R=83.14 cc bar/mol K,

at 77K and applying, for pv/RT=n,

$$\frac{40\ bar\ *\ 215cc}{(83.14\ cc\ bar/mol\ K)\ *77K}$$

= 1.34 mol or and additional 2.69 gm H_2

Add this to the 35 gms adsorbed H_2 so get ~38 gm/liter total

Our "1 liter tank" has a total adsorbed and gas volume density of 38g H_2/600gm AC/liter or 6wt%

A tank with 5kg capacity should then have an interior volume of ~132 liters.

Applying this analysis to IRMOF-1

Total density is 0.6gm/cc and skeletal density is 2.9gm/cc.

In 1 liter, 600gm/2.9gm/cc -> 0.2 liters of skeletal density of IRMOF.

Assume 5wt%storage => 32 gms hydrogen stored and assume this 32 gms occupies ~0.46 liters of "adsorbed" space.

Add this 0.46 liters of 'adsorbed' H_2 to 0.2 liters of IRMOF skeletal density and have 0.34 liters "free" volume to apply gas law to get an additional 4.2 gms H_2 so ~36 gms total in 1 liter (~5.6wt%) or

139 liter interior volume for 5 kg storage.

A 135 liter volume containing no sorbent under these same conditions would hold only 1.7kg of H_2, not 5 kg as with the sorbent, showing the importance of physisorbents under these conditions in improving volumetric densities.

Publications and Presentations

"Saturation of Hydrogen Sorption in Zn Benzenedicarboxylate and Zn Naphthalenedicarboxylate," A. Dailly, J. J. Vajo, and C. C. Ahn, J. Phys. Chem. B Lett., **110**, 1099, 2006.

"Hydrogen cryo-adsorption; comparing low pressure and isosteric heats", C. C. Ahn, invited presentation, American Physical Society Spring Mtg, Baltimore, (March 2006).

"Surface Area Dependence of Hydrogen Gravimetric Density in Carbon Aerogels," H. Kabbour, A. Saulnier, T. F. Baumann*, J. H. Satcher, Jr.* and C. C. Ahn, Electrochemical Society Spring Meeting, Denver, (May 2006).

Manuscript in preparation for 2006 by invitation of the editorial board.
"Hydrogen adsorption in carbon-based materials with a view to transportation applications," to appear in Materials Science Engineering Reports, a review only journal published by Elsevier.

Critical Assumptions and Issues

- Upper surface area limits of carbons measured to be ~3100m^2/gm, imposing upper limits on gravimetric density on basis of known carbons.

- Optimal pore size needs to be in the micro-pore regime (most high surface materials in the meso-porous range >2nm). Synthesizing a material with a small pore size distribution may be difficult.

- Substitutions of constituents to improve adsorption enthalpies need to be accomplished in a way that maintains a high enthalpy across the full pressure range of gravimetric densities.