Enhanced Hydrogen Dipole Physisorption: Constant isosteric heats and hydrogen diffusion in physisorbents

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Caltech

May 20th, 2009

Project ID #STP_27_Ahn

Overview

Timeline

- Project start date:
  October 1, 2004
- Project end date:
  January 31, 2010
- Percent complete: 80%

On board hydrogen storage Barriers and Targets

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

(N) Low temperatures that sorbent-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 FY08
  - DOE share $175k
  - Contractor share $43.5k
- Funding for FY09
  - DOE share $175k
  - Contractor share $43.5k

Partners

Interactions/collaborations:

J. J. Vajo, HRL Laboratories

J. Reiter, J. Zan, Jet Propulsion Lab.

T. Baumann, J. Satcher, Jr., J. Herberg,
          Lawrence Livermore Natl. Lab.

Yun Liu, Craig Brown, Dan Neumann, NIST

R. Hauge, J. Tour, Rice University

D. Geohegan, ORNL

T. Gennett, L. Simpson, NREL

Relevance

- Kinetics of molecular H_2 physisorption can be relatively fast but adsorption enthalpies typically close to thermal energies requiring low temperatures.
- Past work concentrated on synthesizing and evaluating maximal surface area sorbents (maximizing number of sorption sites), necessary for high gravimetric molecular H_2 storage.
  - Activated carbons, aerogels and metal organic frameworks effective, if not optimized, candidate materials as they presently work best at 77K temperature and pressures of 30 to 40 bar with sorption enthalpies of ~4-8 kJ/mole (from our work, presently at 5.8 wt% surface excess at 77K for a 3300 m^2/gm surface area activated carbon, if total including free volume taken into account, gravimetric density closer to 10 wt%).
- Typical sorbents a combination of micro (<2 nm) and mesoporous (2 to 50 nm) microstructures. Enhancement of microporosity in addition to surface area necessary in order to maximize volumetric density. Typical physisorbent volumetric densities presently ~38 gm/liter at 77K).
  - Enhancement of sorption enthalpy accompanies small pore size but pore distribution needs to be determined for thorough assessment.

Approach

- Synthesis of coordinated polymer (framework) structures via normal solvo-thermal routes.

- Evaluation of aerogel properties in collaboration with LLNL.

- Evaluation of microporous activated carbon properties.

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

- Residual gas analysis using volumetric Sieverts with collaborators at JPL.

- Thermodynamic evaluation of sorption enthalpies via Henry's law region of isotherm and/or isosteric enthalpy of adsorption.

- Neutron scattering (diffraction and inelastic) of promising systems in collaboration with NIST.

Technical Accomplishments and Progress: Pore Size Distribution and Adsorption Enthalpy in Activated Carbon Fibers
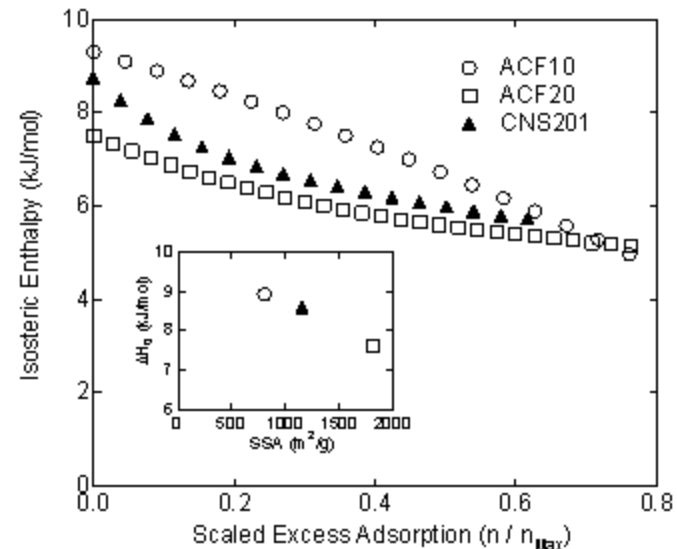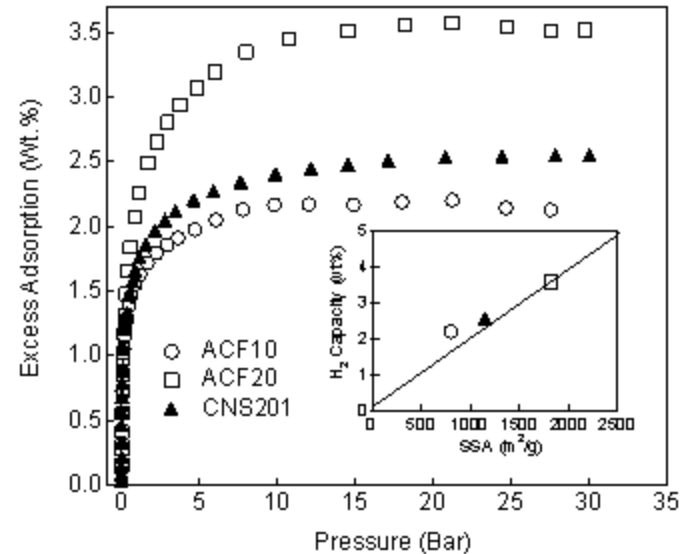
- Analysis completed on CNS-210 coconut based activated carbon and compared to Kynol® activated carbon fibers ACF-1603-10 and 20 (presented last year).

- Lower surface area (shorter activation process) correlates to greater percentage of smallest micropores (that are important for maximizing H_2 volumetric adsorption).

- Minima near 0.6 nm and 1.0 nm probably artifacts of density functional theory (DFT) models.

- Pore size/distribution assessment critical for H_2 sorption analysis in order to maximize DoE volumetric

- Improvements on these models critical to better evaluate structure of synthesized microporous structures.

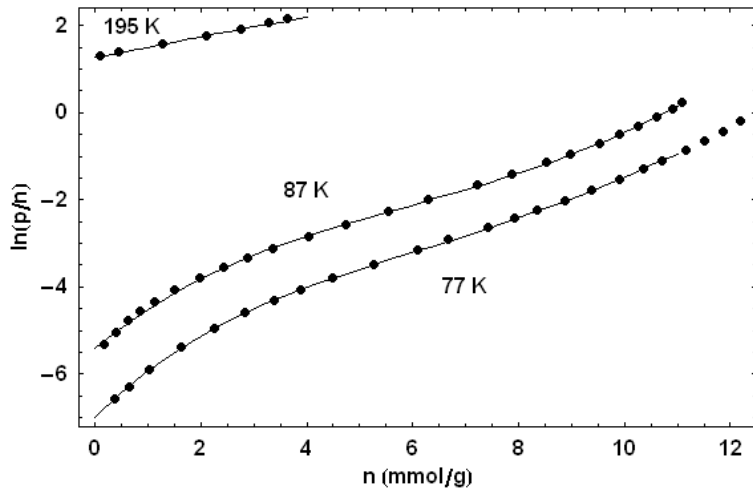| Sample	Surface Area (m^2/g)
ACF-1603-10	801
ACF-1603-20	1817
CNS-201	1158

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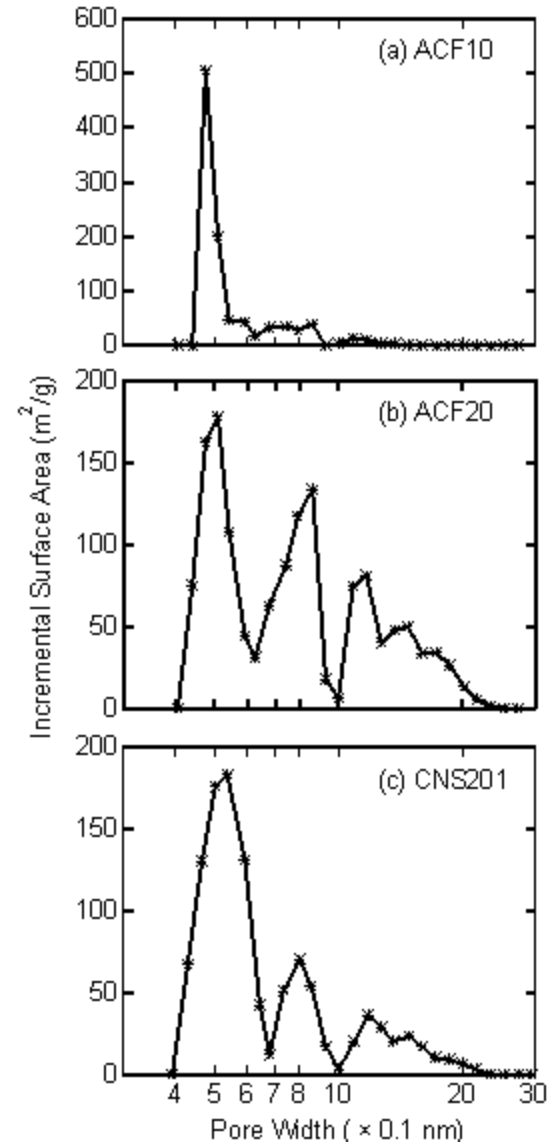
Technical Accomplishments and Progress: Micropore vs. Edge Termination Sites

- H_2 adsorption capacity at 77 K approximately proportional to N_2 BET surface area.
- Smaller surface area samples have a larger percentage of micropore adsorption sites (with larger ΔH).
- Larger surface area samples have more edge termination sites (smaller ΔH).
- Isosteric heat is plotted against the *scaled* surface excess adsorption, to account for differences in the maximum H_2 adsorption capacity. ACF-10 isosteric heat decreases with coverage (initial analysis last year suggested constant heat, see next slide).
- We believe now that isosteric heat decreases should be expected in all <u>unmodified</u> microporous materials unless the pore size has an extremely narrow and small size.
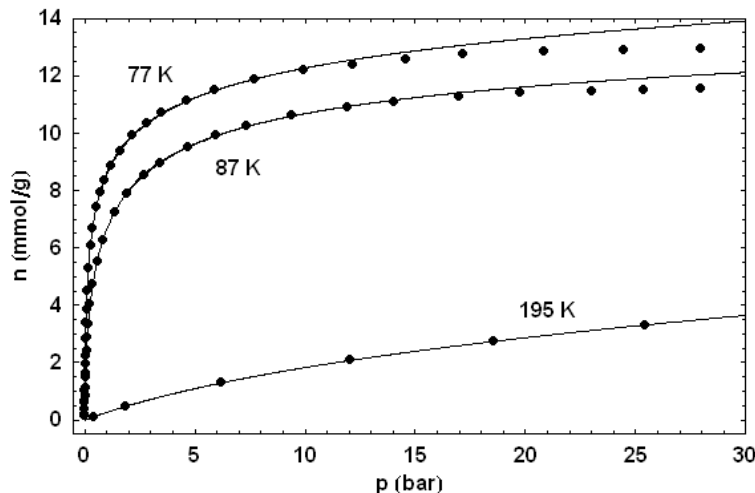
- Continuum of data points needed for enthalpy analysis. Real data taken in increments so data interpolation necessary.
- We have improved our enthalpy analysis of H_2 adsorption isotherms by use of a fit to a model-independent, virial-type equation.[1]
- Model must reduce to Henry's law ($n = K_H p$) in the low-coverage region

$$\ln p = \frac{1}{T} \sum_{i=0}^{l} a_i n^i + \sum_{i=0}^{m} b_i n^i + \ln n$$

- Equation fit simultaneously to 77, 87 and 195 K data.
- Fitting parameters $\{a_i, b_i\}$ are temperature independent
- Zero coverage enthalpy given by $\Delta H_0 = -R a_0$
- Isosteric heat calculated from:

$$\Delta H = -R \left[\frac{\partial \ln p}{\partial (1/T)} \right]_n = -R \sum_{i=0}^{l} a_i n^i$$

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[1]J. Jagiello et al., Chem. Eng. Sci., Vol. 44, No. 4, pp. 797-801 (1989)

- Slit pore regarded as best micropore geometry for sorption. Alkali intercalated graphites at present, best mimic ideal slit pore geometries. Property assessment of these materials enables us to probe effects of large adsorption enthalpy:
  - 9 kJ/mol to 13 kJ/mol (constant)
- We note effect of steric hindrance on physisorption kinetics
  - Two-dimensional model used within alkali metal layers
- Second stage alkali-metal, graphite intercalation compounds MC_{24} (M = K, Rb, Cs)
  - But sluggish adsorption/desorption near saturation, i.e. $MC_{24}(H_2)_2$, implications for refueling time in engineering systems.
- Homogenous adsorption sites
  - Uniform isosteric heat needed for higher, constant temperature operation, of importance for engineering systems.
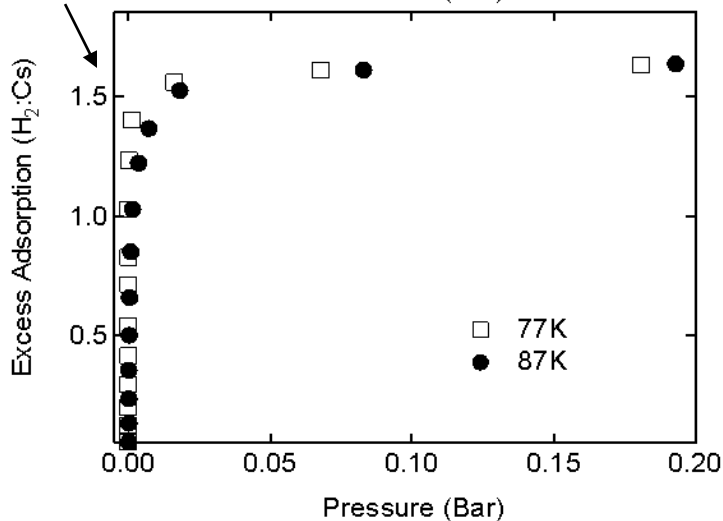
K: 5.4 Å
Rb: 5.7 Å
Cs: 5.9 Å
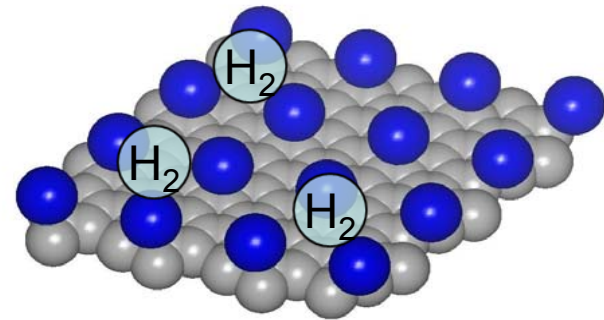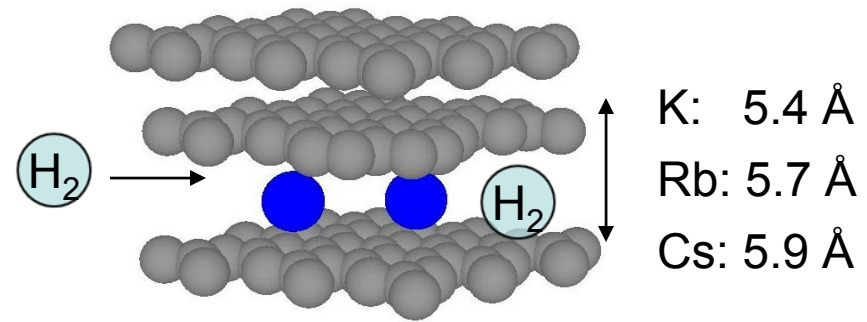
Technical Accomplishments and Progress: Adsorption of H_2 in CsC_{24}: Effect of large sorption enthalpy

sluggish kinetics

Low pressure region expanded
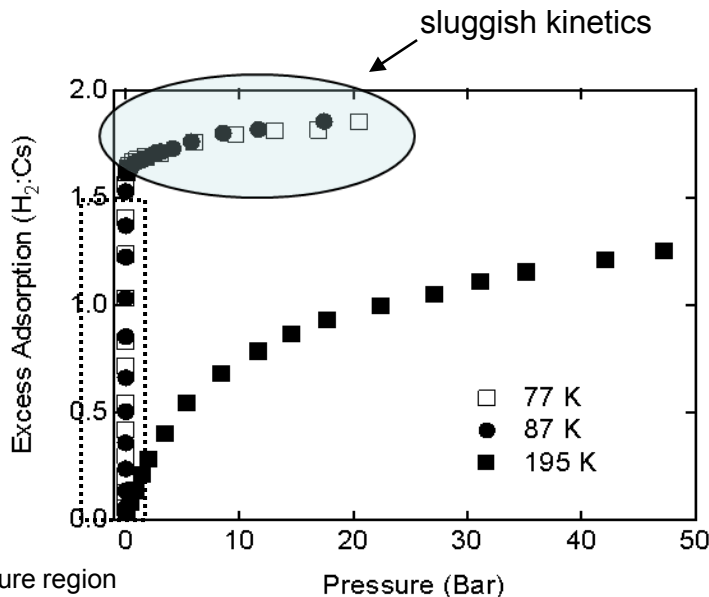
- We show that over 50% of the 77 K capacity is attained at 195 K at modest pressures, empirically confirming the merit of high ΔH as a materials discovery goal. This might be compared with the microporous carbon CNS201 where ~1/3 of the maximum hydrogen loading is seen under similar conditions.
  - $\Delta H_0 \approx 13$ kJ/mol (difficult to measure accurately due to steep isotherms at 77 and 87 K).
  - Efficient hydrogen delivery and kinetics from cycling between 2 – 40 bar at 195 K
  - Poor hydrogen delivery at 77 and 87 K above 2 bar due to steep isotherm, typical of high initial isosteric heat (see lower-left plot).
- Sluggish kinetics (days to reach equil.), limit adsorption above 1.5 (H_2:Cs mole ratio)
  - Steric effects (2D geometry, volume excluded by Cs).
  - Most H_2 adsorption sites are filled, resulting in slow H_2 long-range diffusion. Implications may affect other modifications designed to increase ΔH in graphite based sorbents.

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• To understand diffusion behavior in this model slit pore, especially sluggish kinetics seen at high hydrogen loadings, we employed quasielastic neutron scattering collected on High Flux Backscatter Spectrometer (HFBS at NIST) to determine H_2 diffusion characteristics (fig. at upper right, peaks scaled to equal height).

- Good energy resolution, sensitive to slow processes (long-range diffusion).
- Spectra at small Q probe larger distances (reflects 2D steric effects and suppression of long-range diffusion).

• Large suppression of quasi-elastic scattering in $CsC_{24}(H_2)_{1.5}$ (top right fig.) relative to lower loadings.

- Consistent with kinetically limited adsorption at high loadings.

• Intensity at elastic position ($h\omega=0$, lower right fig. showing intensity at elastic position) shows fast decrease beyond specific temperatures:

- Distinct from Debye Waller factor
- Consistent with decrease in elastic scattering and increase in quasielastic scattering (diffusion of H_2).
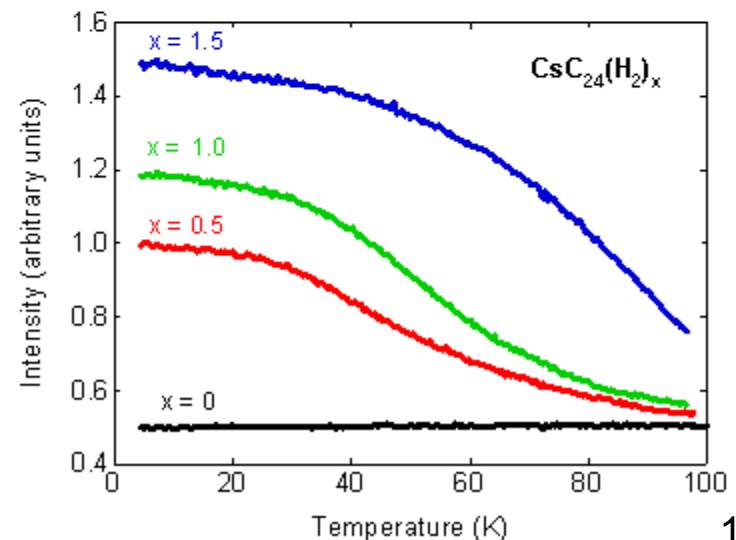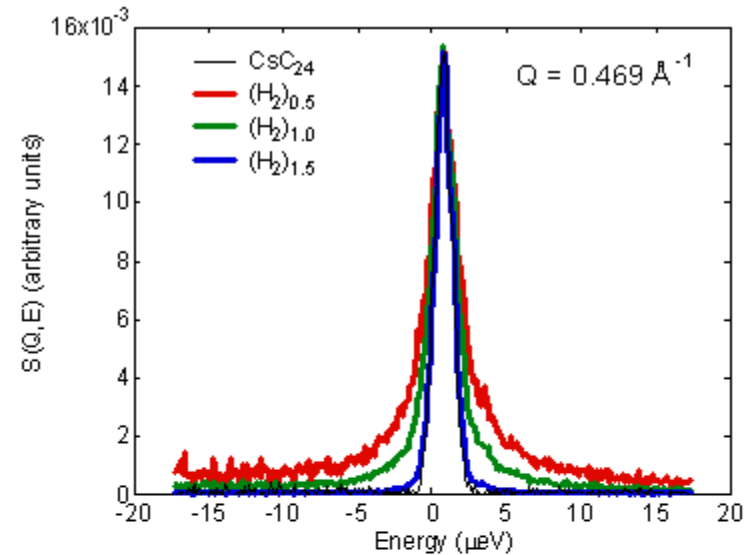
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- Sorbents with constant isosteric heat of greatest value from engineering perspective as this allows storage tanks to run with the need to consider only pressure excursions and not temperature excursions.

- Intercalated carbons the only systems we are aware of that have constant isosteric heats.

- Assessing the nature of deviation from ideal "Langmuir" adsorption isotherms at low coverage is shown in this work.

  – Expansion of interlayer spacing in conjunction with adsorption in KC_{24}

- Homogeneous sorption sites

  – Relatively constant isosteric heat in comparison to unmodified microporous carbons, here equal to 8.5 kJ/mol in the zero coverage limit. (4 to 6 kJ/mole typical in carbon materials).

  – Saturation capacity the same at 77 and 87 K.

- Kinetic limitations of adsorption at high H_2 filling present above ~1.7, but not as pronounced as in CsC_{24}
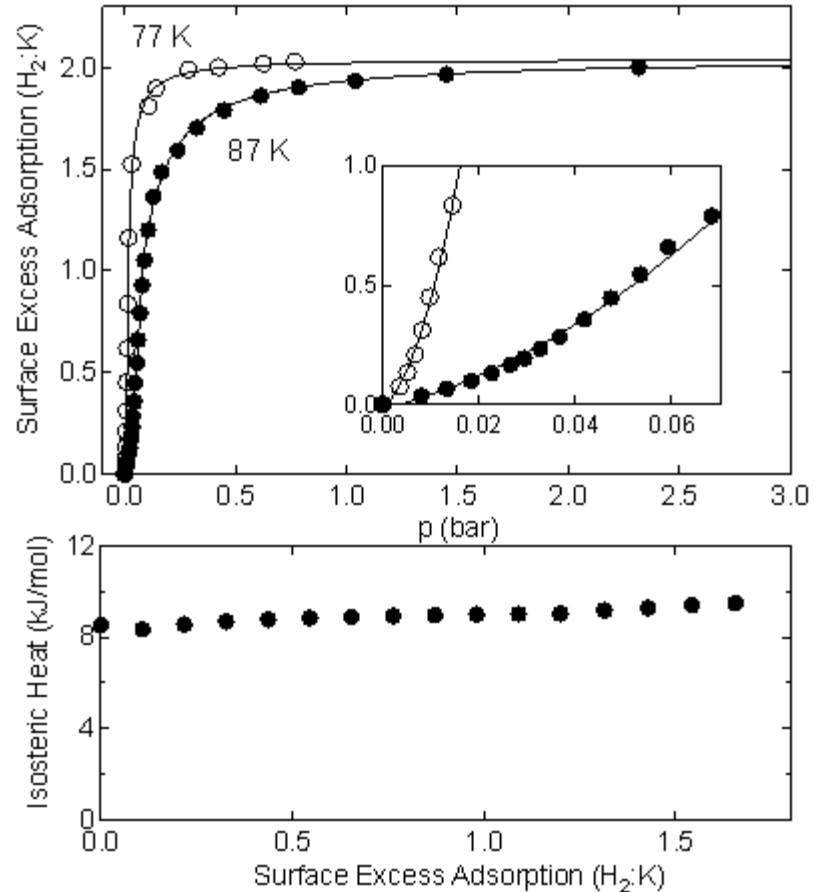
- Diffusion time study for hydrogen adsorption necessary as it relates to hydrogen refueling times.

- Two distinct hydrogen diffusion time-scales for KC_{24} presented here: one fast and one slow are presented in the plots at the right. Note that the x-axis time scales for these plots are different.

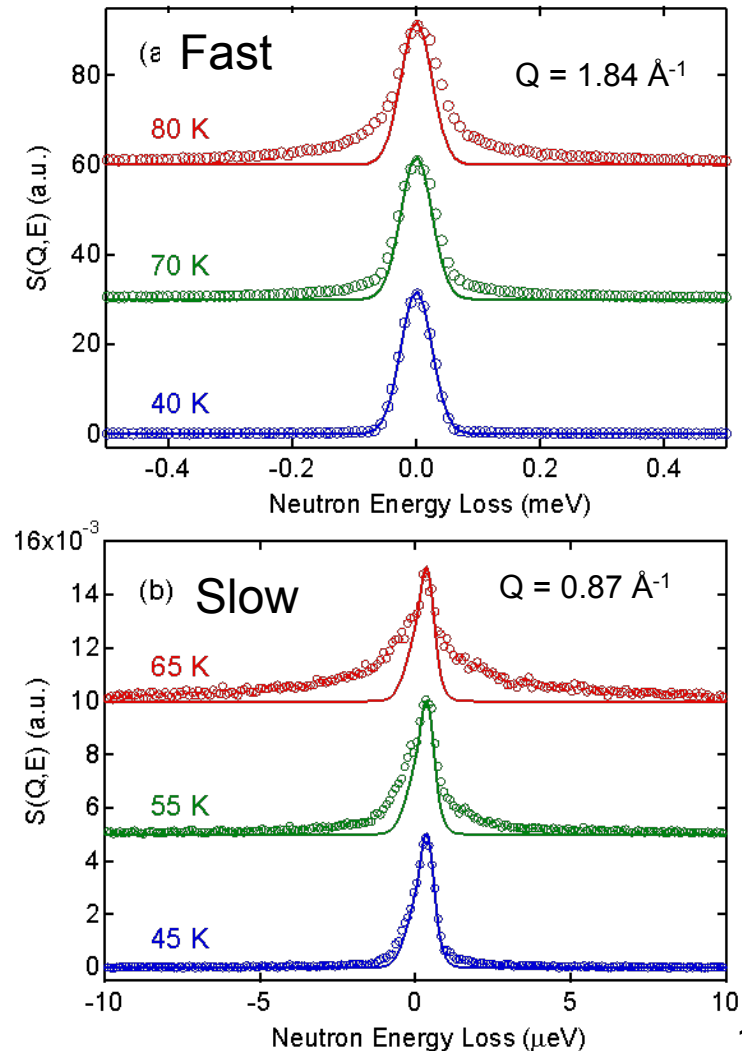- Characteristic times follow an Arrhenius relation:
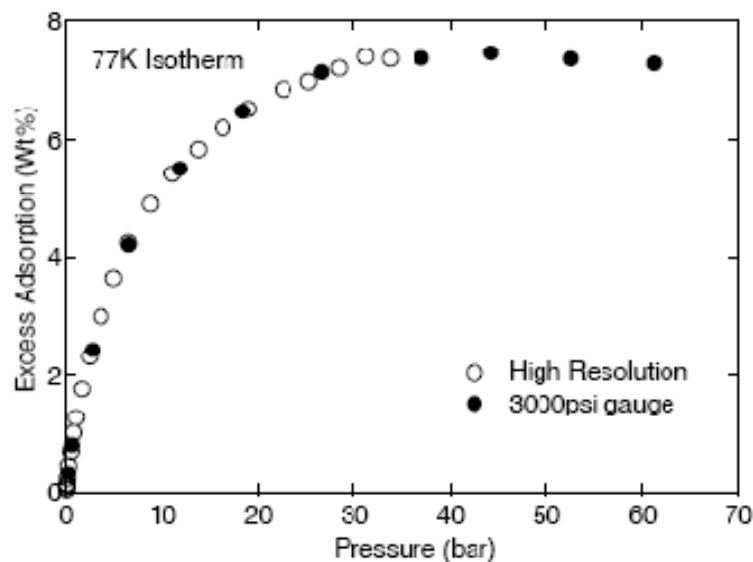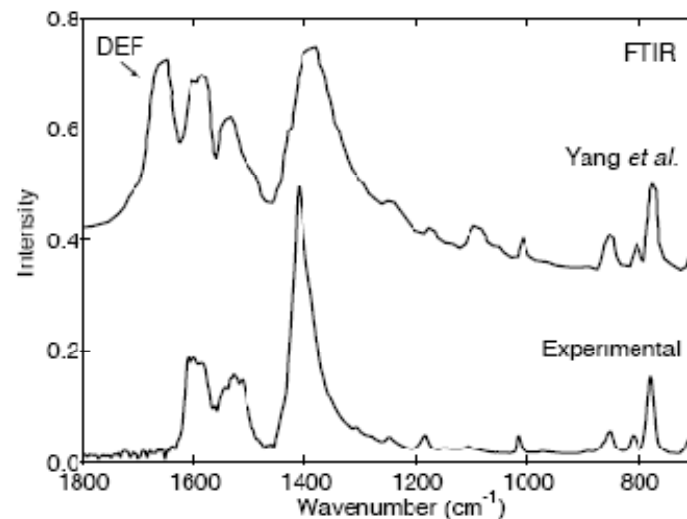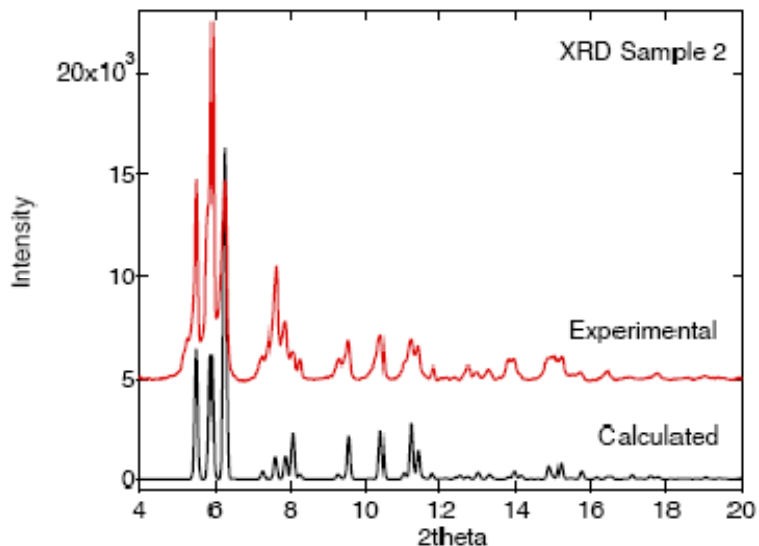
$$\tau = \tau_0 \exp[- E_a / k_B T]$$

where

$$\tau_0^{fast} = 1.0 \pm 0.1 \text{ ps}$$

$$\tau_0^{slow} = 21 \pm 2 \text{ ps}$$

- Fast process are presumably related to short-range motions.

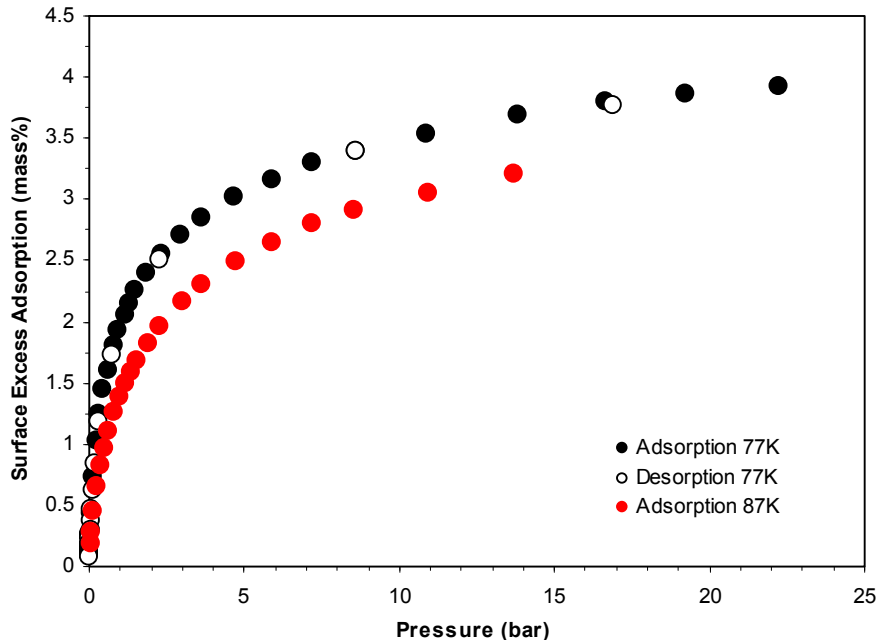- Slow process may originate from long-range diffusion.

(a) Fast — $Q = 1.84 \text{ Å}^{-1}$; 80 K, 70 K, 40 K; $S(Q,E)$ (a.u.) vs Neutron Energy Loss (meV)

(b) Slow — $Q = 0.87 \text{ Å}^{-1}$; 65 K, 55 K, 45 K; $S(Q,E)$ (a.u.) vs Neutron Energy Loss (μeV)

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Technical Accomplishments and Progress: Synthesis of MOF-177 for neutron scattering studies

XRD Sample 2 — Intensity vs 2theta. Experimental and Calculated curves.

FTIR — Intensity vs Wavenumber (cm^{-1}). DEF, Yang et al., Experimental.

77K Isotherm — Excess Adsorption (Wt%) vs Pressure (bar). High Resolution (open circles), 3000psi gauge (filled circles).

- 12 batches of MOF 177 synthesized for neutron scattering studies at NIST in order to understand hydrogen interaction at sorption sites (this material at present shows one of the highest gravimetric densities of 7wt% at 77K but a volumetric density of only ~32gm/liter).

- X-ray diffraction data of our materials consistent with calculated peak positions.

- FTIR data consistent with removal of solvent.

- Our isotherm data does show 7wt% hydrogen uptake.

- Neutron scattering studies presently underway

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- High surface area materials are characterized by graphitic edges with zig-zag or arm chair geometries with hydrogen, hydroxyl or oxygen terminations.

- Initial studies employed to assess thermodynamic changes associated with replacement of edge terminated species in AX-21 with F terminations.

- We measure a differential zero-coverage adsorption enthalpy of 6.3 kJ/mol, comparable to as-received AX-21 starting material.

- Further processing underway at Rice to better evaluate extent of F substitutions in this system, but initial efforts at F substitution probably require other analytical techniques to assess the extent of base species replacement at graphititc edges.

Technical Accomplishments and Progress: Initial evaluation of chromia aerogel enthalpies (with T. Baumann, LLNL)

- Literature suggests that crystalline chromia has a large affinity for hydrogen sorption. Our initial analysis of an amorphous chromia aerogel, prepared by T. Baumann, has a differential zero coverage enthalpy of 5.7 kJ/mol.

- At upper right are adsorption (solid data points) and desorption (open data points) isotherms taken at 77 and 87K

- Errors in data due to small sample size resulting in <1 mg H_2 adsorbed for the comparatively small surface area of this type of aerogel.

- Of note for this material is that the isosteric enthalpy is nearly constant.

- Larger material quantities synthesized by LLNL are presently undergoing evaluation.
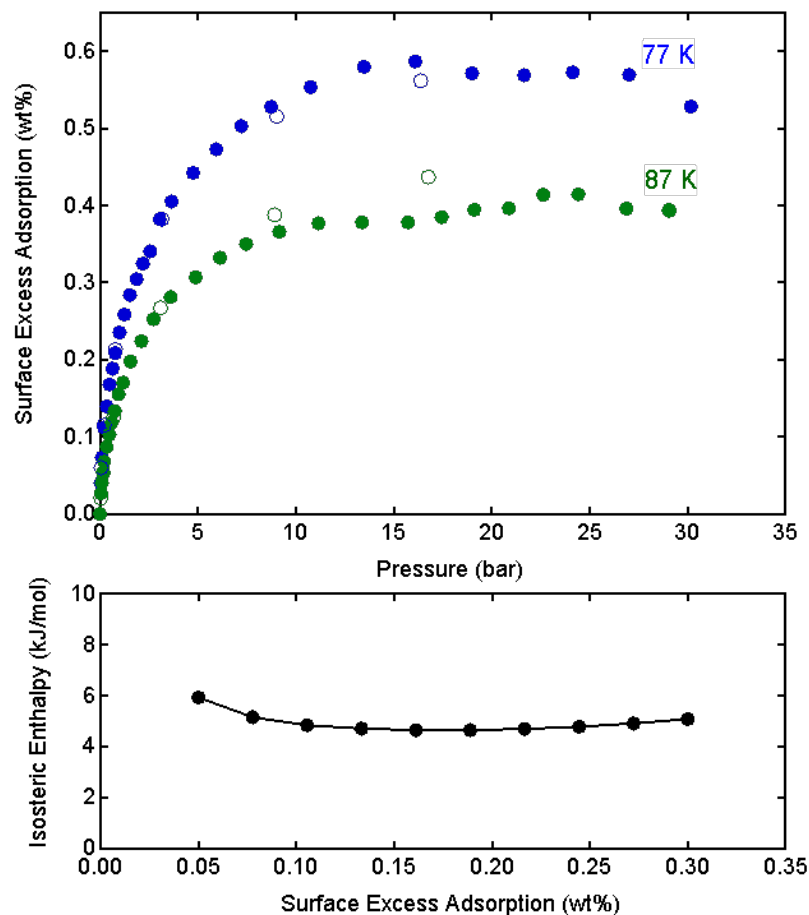
Conclusions:

• Adsorbents with the constant isosteric heats that are needed for simpler storage tank design have been assessed.

• In the intercalated system KC_{24}, a relatively constant isosteric heat of 8.5 kJ/mole H_2 is seen.

• In the CsC_{24} system, a 13 kJ/mole heat is seen and the195K data shows that ~2/3 of the surface excess 77K hydrogen capacity can be obtained when moderate pressures of ~50 bar are applied. This confirms the goal of high ΔH as a materials discovery criterion for sorbent research. The 2/3 surface excess value should be compared to the value of an unmodified microporous carbon which attains only ~1/3 of the 77K maximum value at 195K.

• Diffusion kinetics of hydrogen in these systems are affected by the extent of hydrogen loading with high loadings resulting in slower diffusion. This may be of critical importance in refueling times using materials of this type.

• In work with our collaborators, we have also synthesized a high surface area MOF177 framework for neutron scattering studies. We have also assessed surface excess isotherms and derived isosteric heats for a BF_3 treated activated carbon and for a chromia aerogel. These two efforts are still currently underway.

Collaborations

- John Vajo, HRL Laboratories, TGA analysis of metal modified aerogels and activated carbons

- T. Gennett, NREL (Center partner), surface area and pore distribution analysis and spillover analysis of activated carbons.

- D. Geohegan, ORNL (Center partner), surface area and pore distribution analysis of activated carbons.

- J. Reiter, J. Zan, Jet Propulsion Lab (sub contractor), residual gas analysis of physisorption/desorption gases at high temperature. Software and computer control of Sieverts systems.

- T. Baumann (Center partner), Lawrence Livermore Natl. Lab., carbon and other aerogel synthesis for enthalpy analysis.

- Craig Brown, Dan Neumann, NIST (Center partner), Elastic and inelastic neutron scattering of coordinated polymer (framework) structures.

- R. Hauge and J. Tour, Rice University, (Center partners), BF3 modified activated carbons and metal modified graphites.

- Gavin Walker (Nottingham) and M. Hirscher (Max-Planck, Stuttgart), surface area and gravimetric uptake in activated carbons.

Plans for 2009/2010

- Continued collaboration with Ted Baumann of LLNL on aerogel analysis including chromia work that we have already initiated, in order to better assess the high sorption enthalpies that have been reported previously in the literature

- Continued synthesis and activation of MOF and MIL (Material Institut Lavoisier) and other high surface area structures to improve gravimetric densities. Pursuit of those systems that display homogeneous sorption enthalpies.

- Optimization of pore size/volume in collaboration with J. Tour of Rice University, 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).

Summary of thermodynamic analysis of physisorbents examined during 2008-2009

- Intercalated graphites a working example of hydrogen sorbents with constant isosteric heat.

- Independent synthesis of MOF177 shows 7 wt% surface excess hydrogen loading at 77K but low volumetric density and low sorption enthalpy.

- High ΔH seen in CsC_{24} with high 195K loading offers empirical validation of goal of high sorption enthalpies.

Sample	Gravimetric	Volumetric	ΔH_h (kJ/mole)	ΔH_i (kJ/mole)
MOF-177	7 wt% at 77K	32 kg/m^3	4.5	4.5 to 4
KC_{24}	1.2 wt%	25 kg/m^3	8.5	8.5
CsC_{24}	1 wt%	21 kg/m^3	13	13
Cr_2O_3 aerogel	2.4 wt% (4 wt% tot)	-	8.4	8.5 to 5
AX-21	5.8 wt% at 77K	25 kg/m^3	6	6 to 4

Additional Slides

Henry's law and isosteric heats
Thermodynamically, strict definitions of engineering value
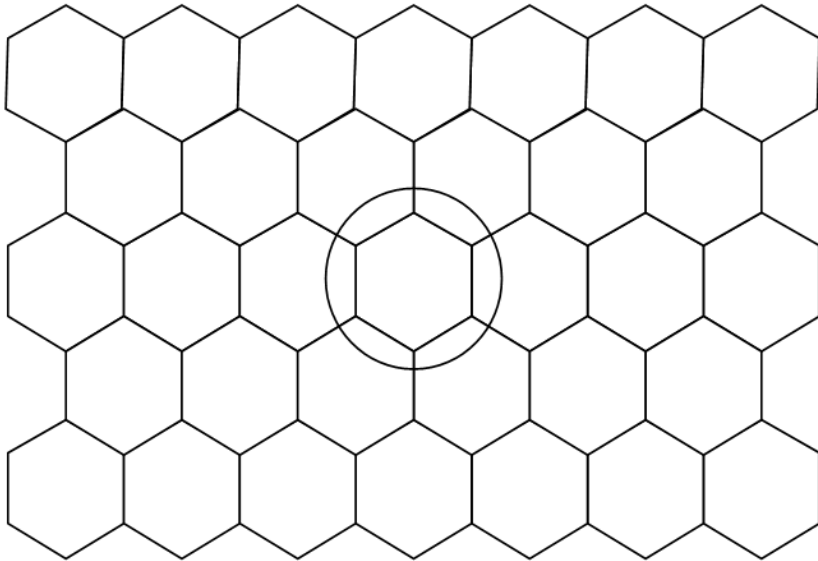
Henry's law region dictated by low coverage, "differential enthalpy of adsorption at zero coverage" so we can assume adsorbate molecules act independently.
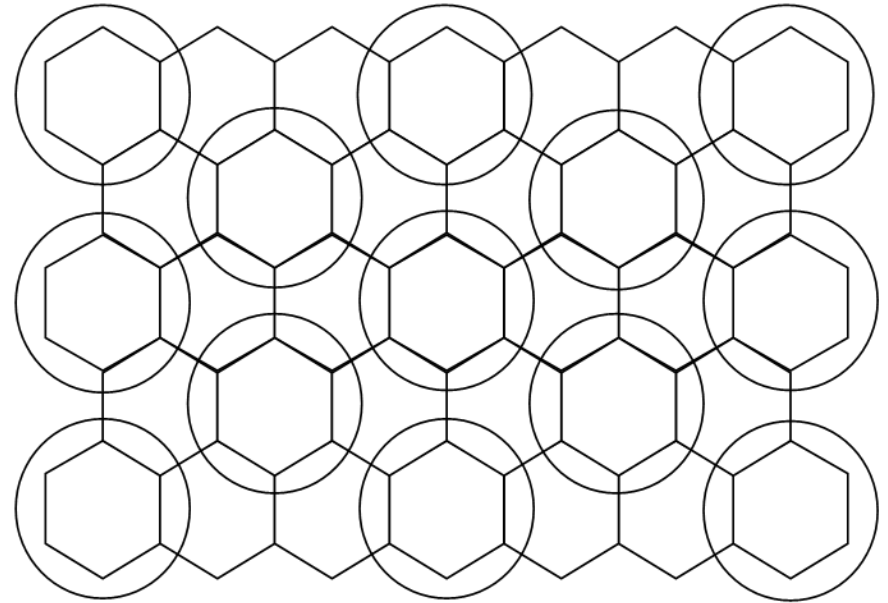
Isosteric heat or, "isosteric enthalpy of adsorption" better reflects change in heat vs coverage.

Real vs Ideal gas behavior at 77, 298 and 573K
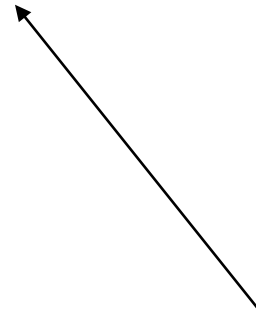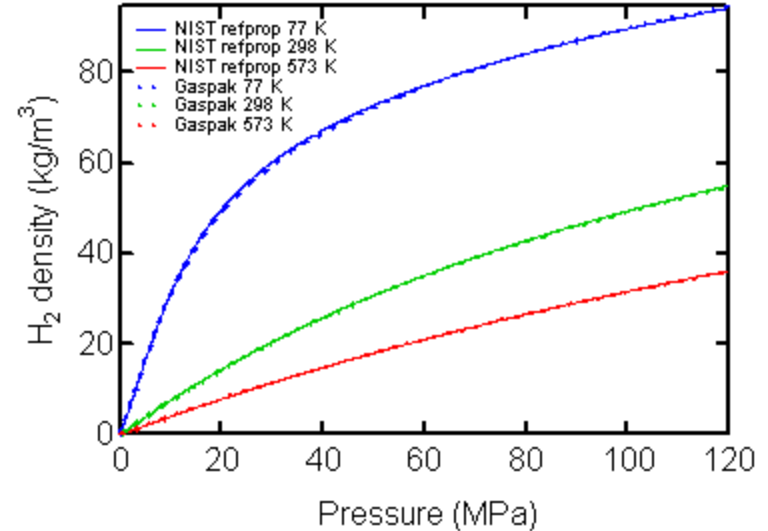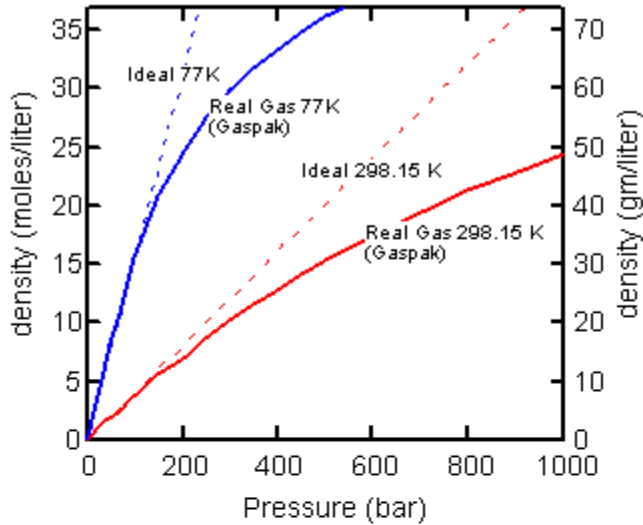

Comparison of Gaspak and Refprop at top.

Gaspak equations here 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.
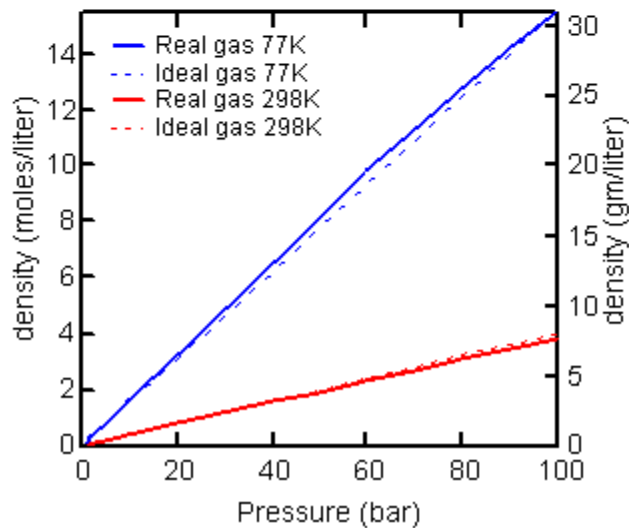
At pressures to 100 bar, real and ideal gas behavior similar for both 77K and RT

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 of surface excess amount.
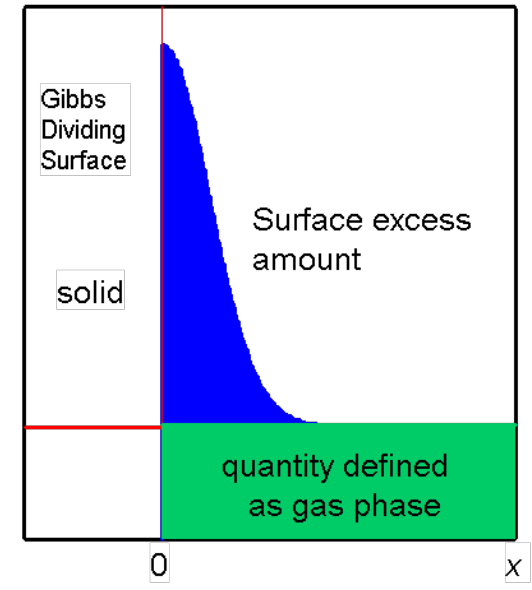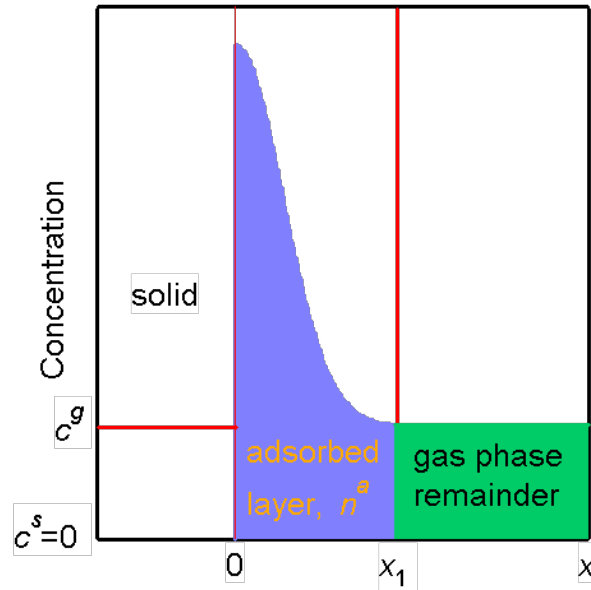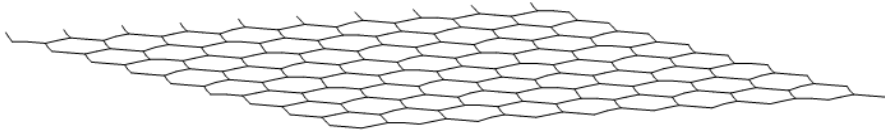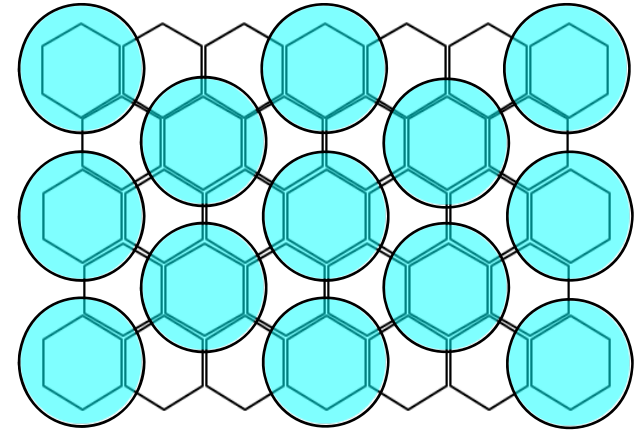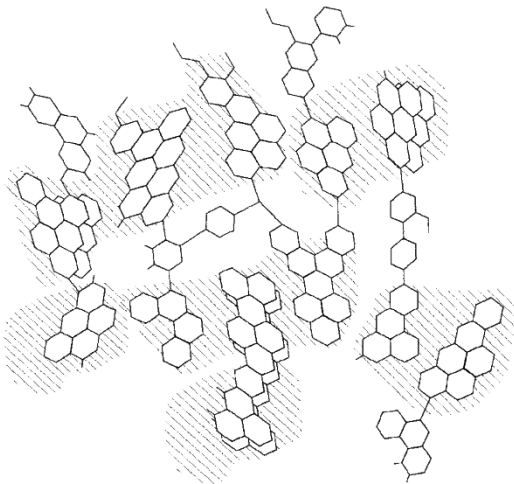
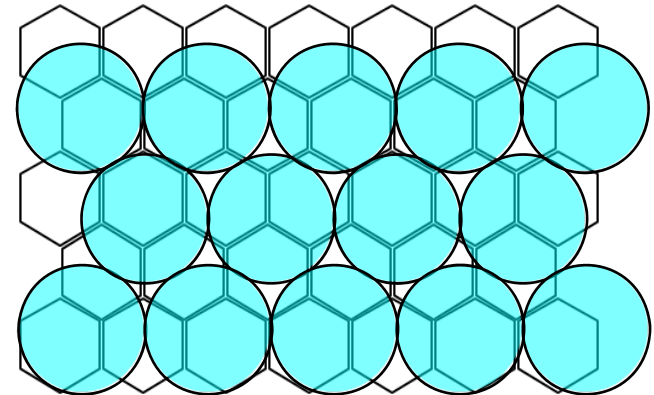LH_2 > surface density > gas law density
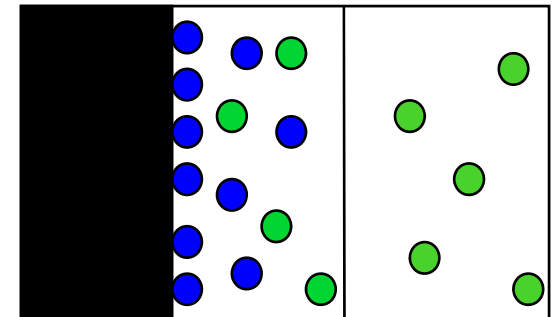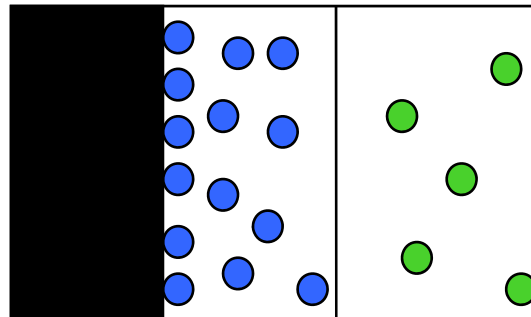
Range of graphitic structures

Theoretical surface area of a graphene sheet is 2630 m²/gm.

Activated carbons can have higher surface areas of >3100m²/gm, edge components important.

Commensurate √3 structure (LiC$_6$) or HC$_3$ => 2.7 wt% (5.4 wt%)

Incommensurate solid H$_2$ on graphite => 3.85 wt% (7.7 wt%).