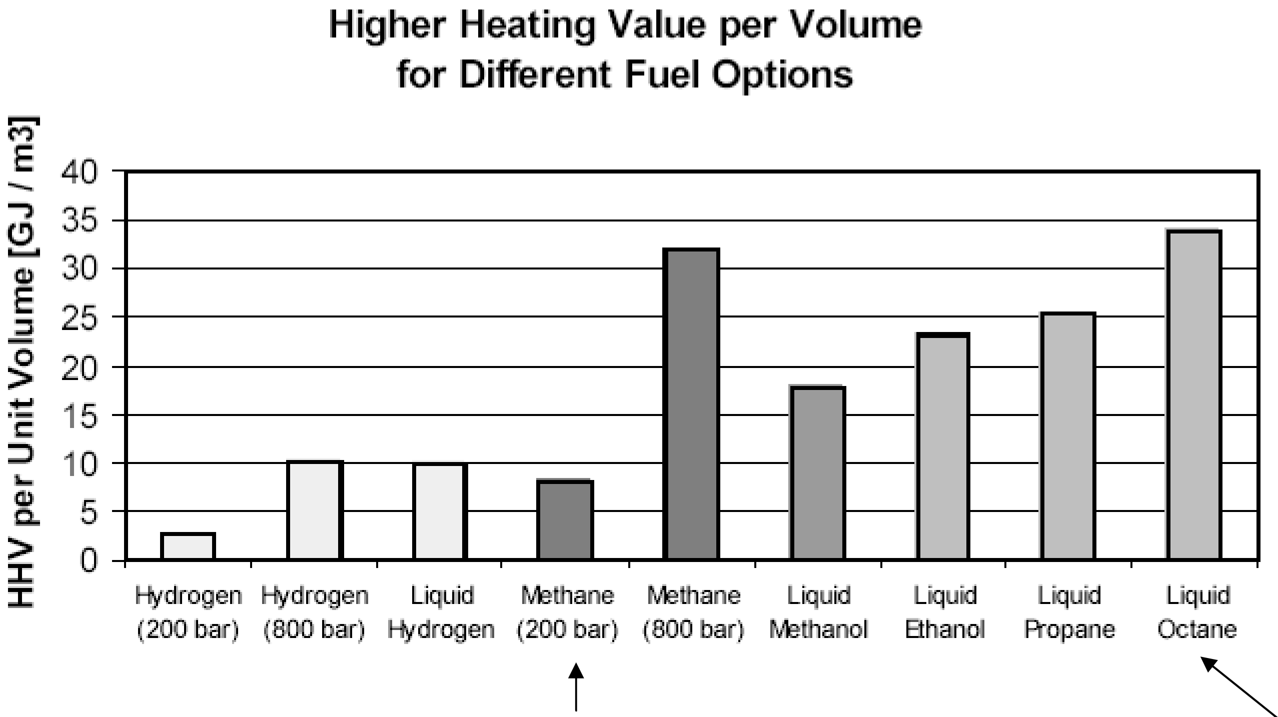
Sustainable Hydrogen and Electrical Energy Storage
6

F.M. Mulder & M. Wagemaker

TU Delft

Comparison liquid and gaseous H_2 with other liquid fuels

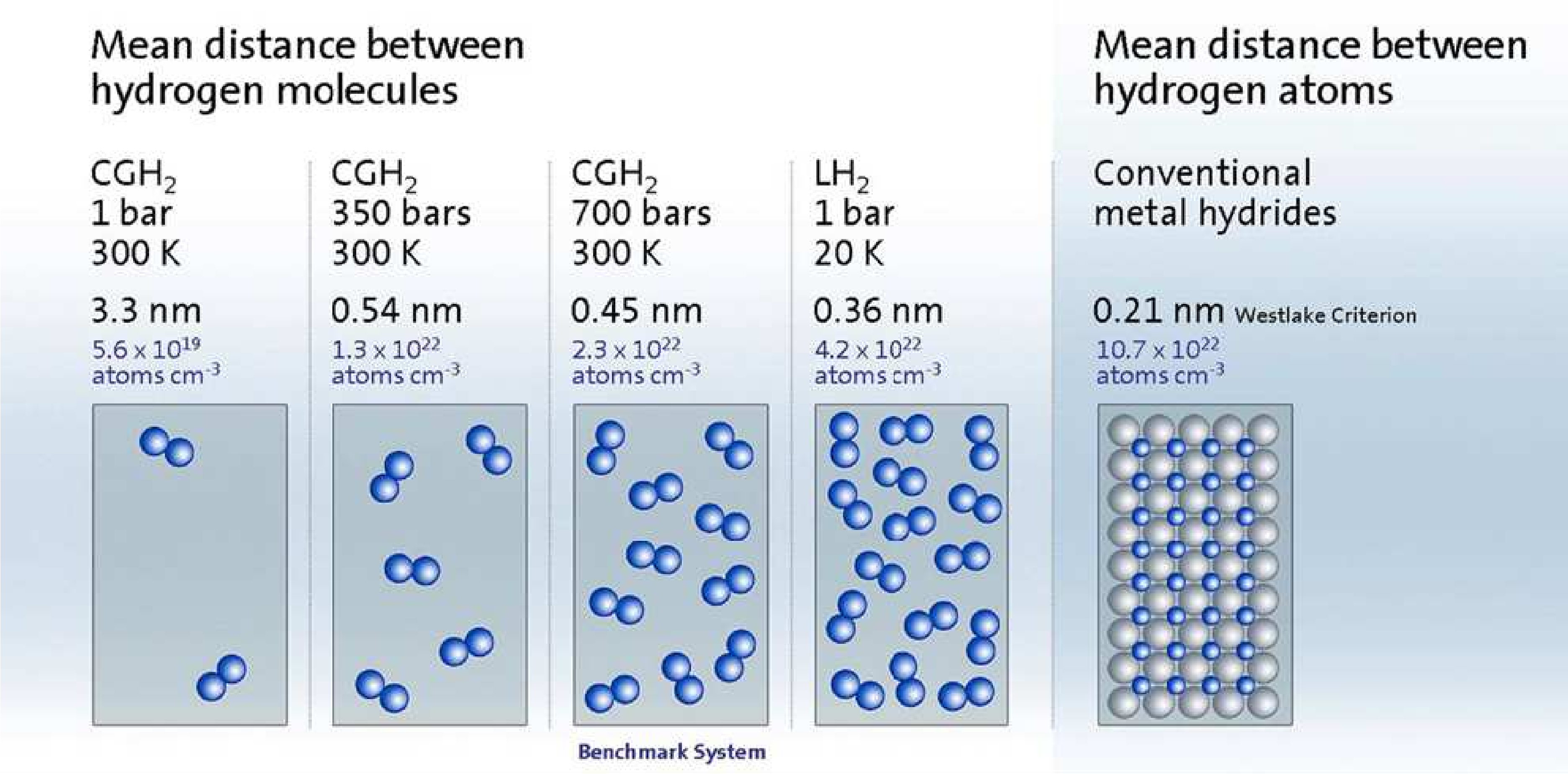


Natural gas

gasoline

Volumetric energy density H_2 is lower than other possible energy carriers

And the other carriers can be contained in more simple conditions



CG: compressed gas, L: liquid

Hydrogen storage

inside materials

You probably have it at home:

in a Ni-MH rechargeable battery

Hydrogen storage requirements

Often the targets of the Department of Energy of the USA are quoted

U.S. DEPARTMENT OF ENERGY

www1.eere.energy.gov/hydrogenandfuelcells/storage/current_technology.html

Hydrogen storage requirements

- High capacity expressed in wt% H_2 of the system
- High capacity in kg H_2/L of the system
- Practical operating conditions (T and P close to RT and 1 Bar)
- Reloadable for many cycles
- Energy efficient
- Fast in loading and unloading
- Safe
- Cheap
- Environmentally sound

See also chapter 9 Gupta

Gupta

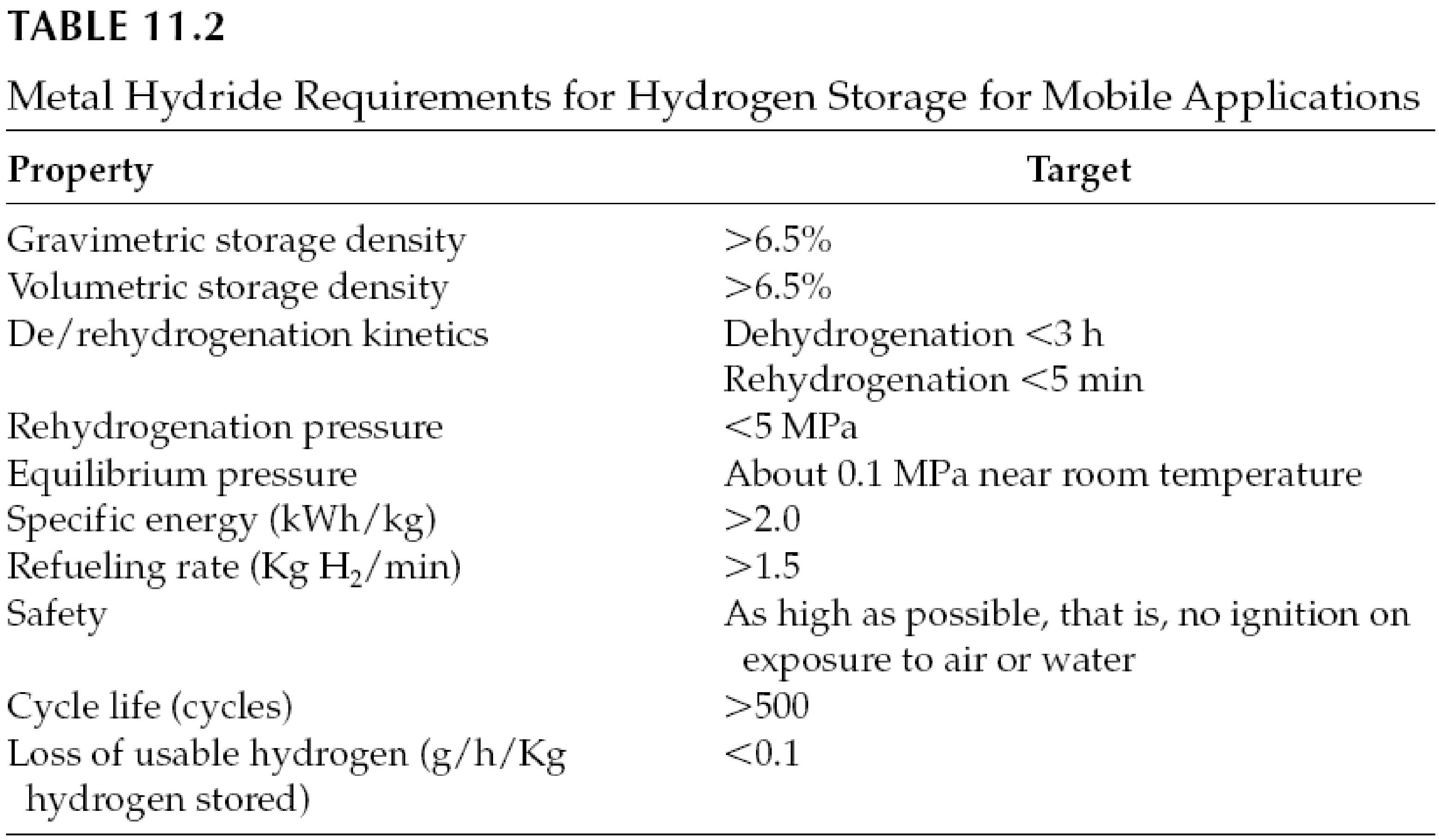


TABLE 11.2

Metal Hydride Requirements for Hydrogen Storage for Mobile Applications

Property	Target
Gravimetric storage density	>6.5%
Volumetric storage density	>6.5%
De/rehydrogenation kinetics	Dehydrogenation <3 h Rehydrogenation <5 min
Rehydrogenation pressure	<5 MPa
Equilibrium pressure	About 0.1 MPa near room temperature
Specific energy (kWh/kg)	>2.0
Refueling rate (Kg H_2/min)	>1.5
Safety	As high as possible, that is, no ignition on exposure to air or water
Cycle life (cycles)	>500
Loss of usable hydrogen (g/h/Kg hydrogen stored)	<0.1

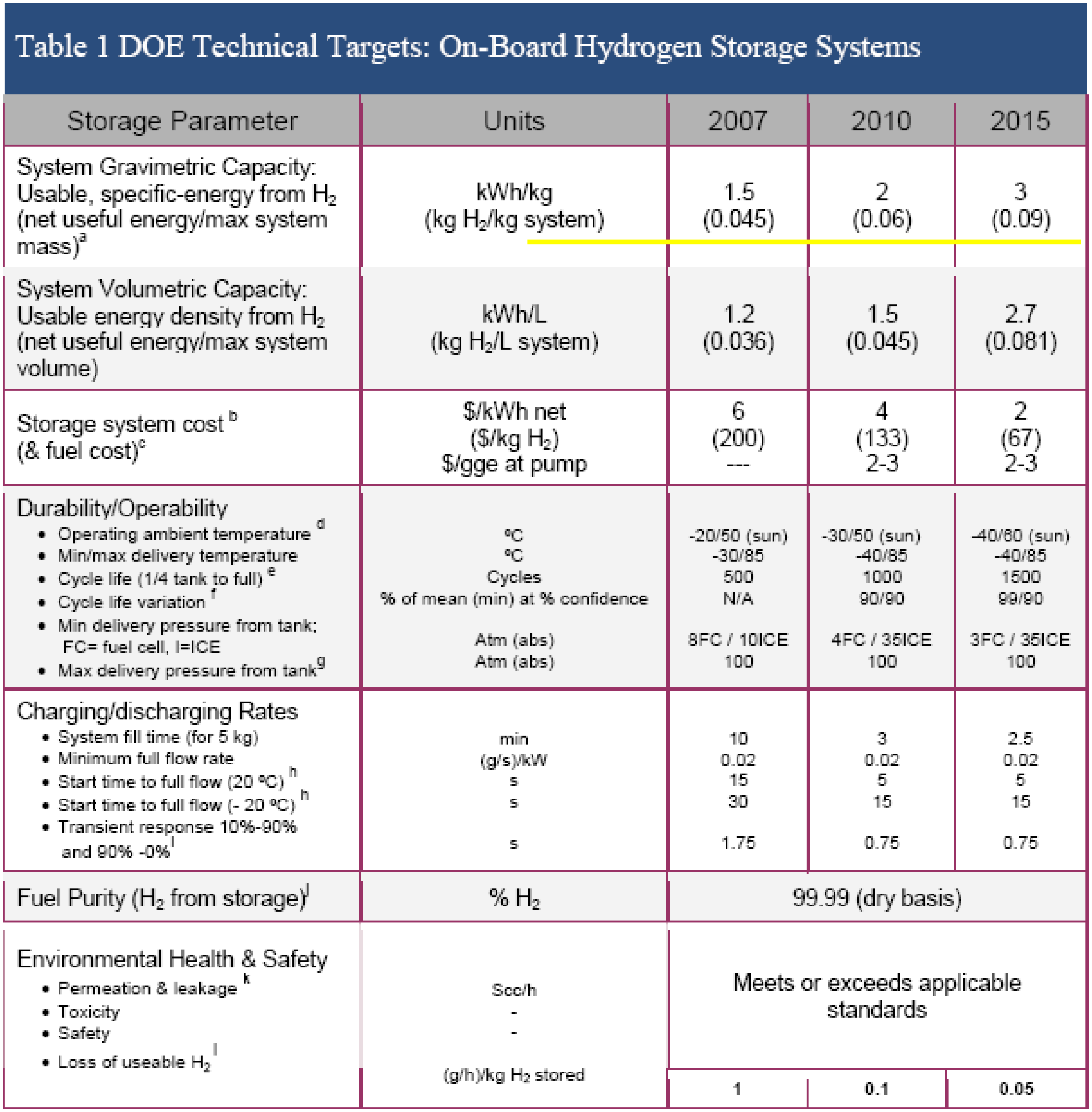


Table 1 DOE Technical Targets: On-Board Hydrogen Storage Systems

Storage Parameter	Units	2007	2010	2015
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass)[a]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	2 (0.06)	3 (0.09)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	1.2 (0.036)	1.5 (0.045)	2.7 (0.081)
Storage system cost[b] (& fuel cost)[c]	\$/kWh net (\$/kg H_2) \$/gge at pump	6 (200) ---	4 (133) 2-3	2 (67) 2-3
Durability/Operability				
• Operating ambient temperature[d]	°C	-20/50 (sun)	-30/50 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-30/85	-40/85	-40/85
• Cycle life (1/4 tank to full)[e]	Cycles	500	1000	1500
• Cycle life variation[f]	% of mean (min) at % confidence	N/A	90/90	99/90
• Min delivery pressure from tank; FC= fuel cell, I=ICE	Atm (abs)	8FC / 10ICE	4FC / 35ICE	3FC / 35ICE
• Max delivery pressure from tank[g]	Atm (abs)	100	100	100
Charging/discharging Rates				
• System fill time (for 5 kg)	min	10	3	2.5
• Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
• Start time to full flow (20 °C)[h]	s	15	5	5
• Start time to full flow (- 20 °C)[h]	s	30	15	15
• Transient response 10%-90% and 90% -0%[i]	s	1.75	0.75	0.75
Fuel Purity (H_2 from storage)[j]	% H_2	99.99 (dry basis)		
Environmental Health & Safety				
• Permeation & leakage[k]	Scc/h	Meets or exceeds applicable standards		
• Toxicity	-			
• Safety	-			
• Loss of useable H_2[l]	(g/h)/kg H_2 stored	1	0.1	0.05

DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles

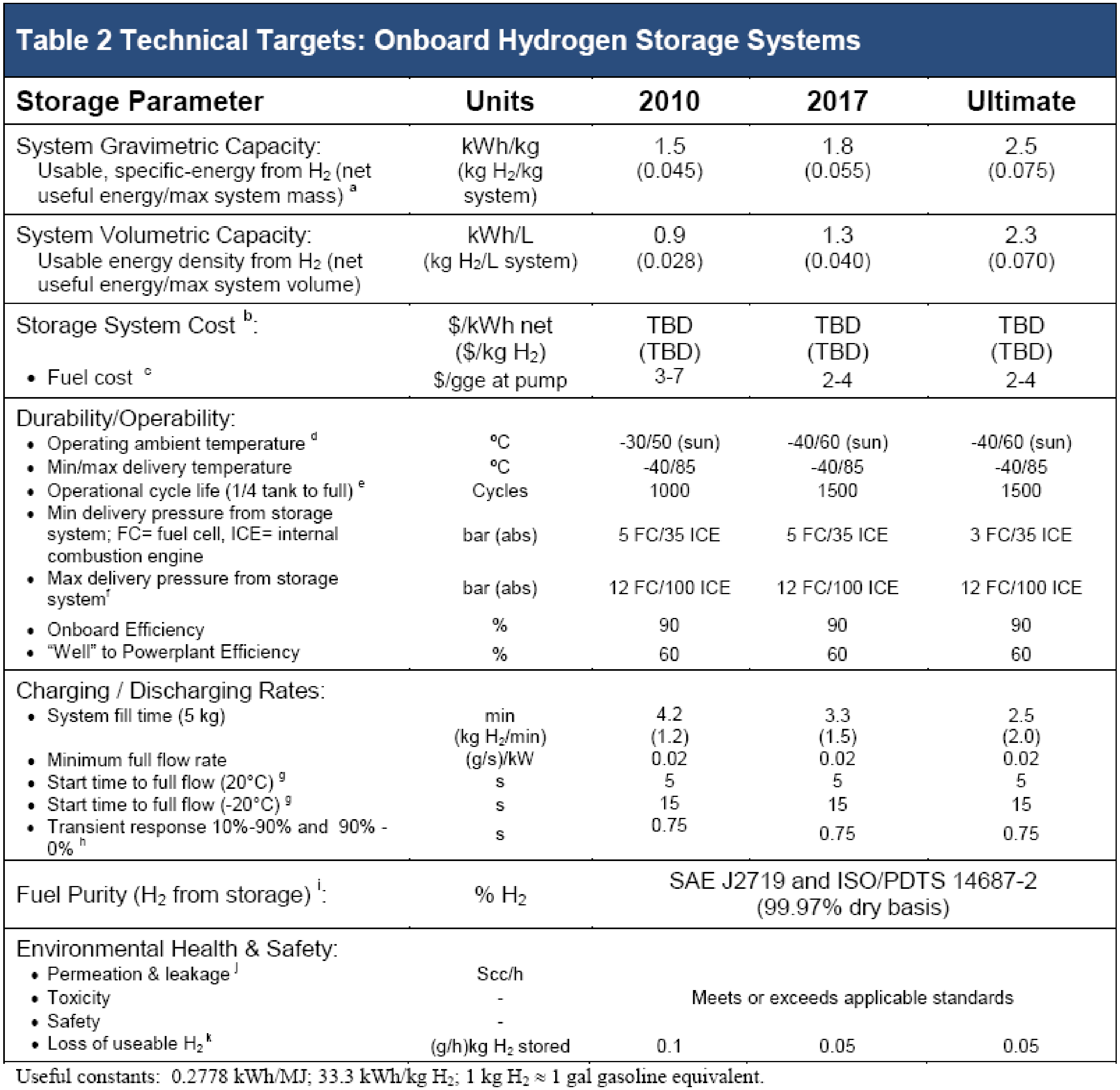


Table 2 Technical Targets: Onboard Hydrogen Storage Systems

Storage Parameter	Units	2010	2017	Ultimate
System Gravimetric Capacity: Usable, specific-energy from H_2 (net useful energy/max system mass) [a]	kWh/kg (kg H_2/kg system)	1.5 (0.045)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	0.9 (0.028)	1.3 (0.040)	2.3 (0.070)
Storage System Cost [b]:	\$/kWh net (\$/kg H_2)	TBD (TBD)	TBD (TBD)	TBD (TBD)
- Fuel cost [c]	\$/gge at pump	3-7	2-4	2-4
Durability/Operability:				
- Operating ambient temperature [d]	ºC	-30/50 (sun)	-40/60 (sun)	-40/60 (sun)
- Min/max delivery temperature	ºC	-40/85	-40/85	-40/85
- Operational cycle life (1/4 tank to full) [e]	Cycles	1000	1500	1500
- Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	bar (abs)	5 FC/35 ICE	5 FC/35 ICE	3 FC/35 ICE
- Max delivery pressure from storage system [f]	bar (abs)	12 FC/100 ICE	12 FC/100 ICE	12 FC/100 ICE
- Onboard Efficiency	%	90	90	90
- "Well" to Powerplant Efficiency	%	60	60	60
Charging / Discharging Rates:				
- System fill time (5 kg)	min (kg H_2/min)	4.2 (1.2)	3.3 (1.5)	2.5 (2.0)
- Minimum full flow rate	(g/s)/kW	0.02	0.02	0.02
- Start time to full flow (20°C) [g]	s	5	5	5
- Start time to full flow (-20°C) [g]	s	15	15	15
- Transient response 10%-90% and 90% - 0% [h]	s	0.75	0.75	0.75
Fuel Purity (H_2 from storage) [i]:	% H_2	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)		
Environmental Health & Safety:				
- Permeation & leakage [j]	Scc/h	Meets or exceeds applicable standards		
- Toxicity	-			
- Safety	-			
- Loss of useable H_2 [k]	(g/h)kg H_2 stored	0.1	0.05	0.05

Useful constants: 0.2778 kWh/MJ; 33.3 kWh/kg H_2; 1 kg H_2 ≈ 1 gal gasoline equivalent.

Newer list with targets: goals are set at less high values

Hydrogen storage requirements (targets 2009)

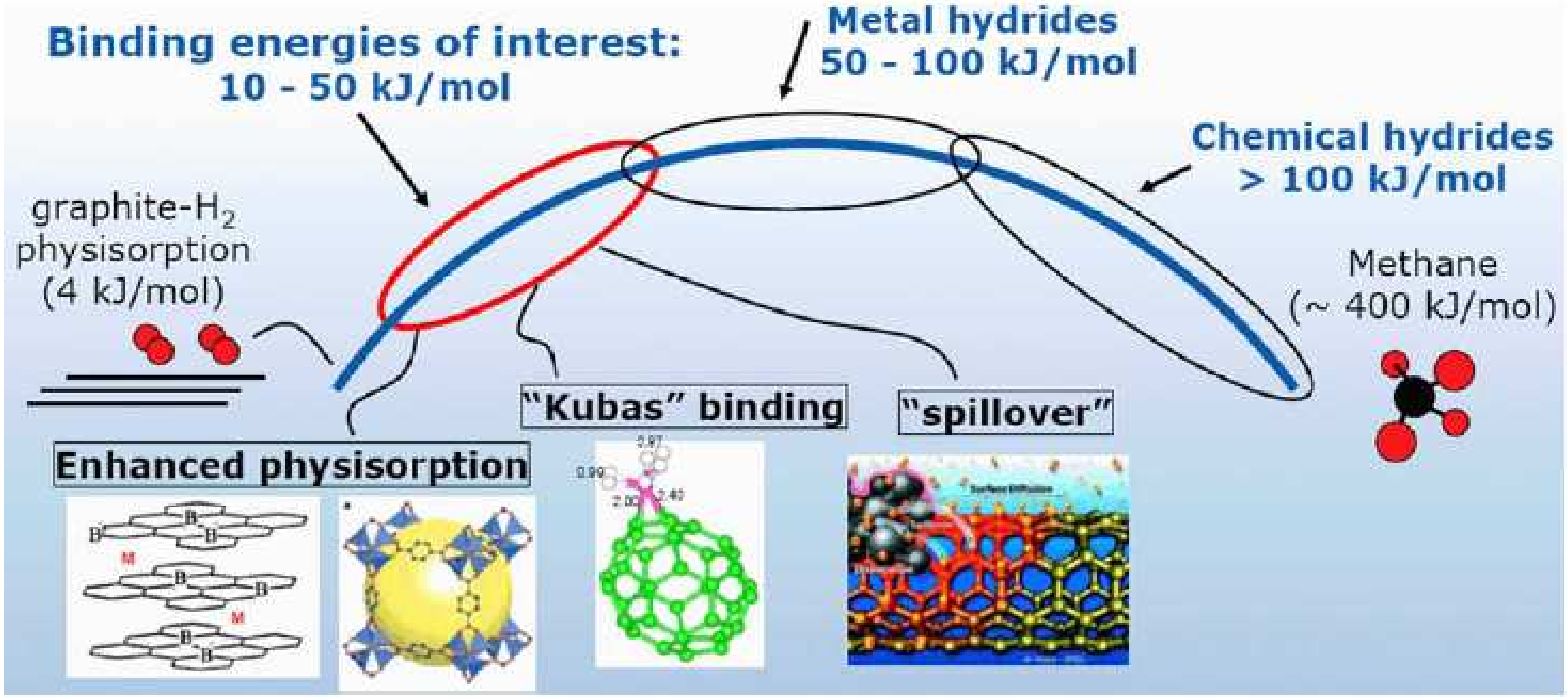
Capacity of the *system* :	0.045, i.e. 4.5 wt%	2010
	0.055, i.e. 5.5 wt%	2017

The system includes container, storage material, tubes, filters, shutters.

However, if in the following capacities of materials are quoted it are capacities of only that material, but in principle also the rest should be taken into account.

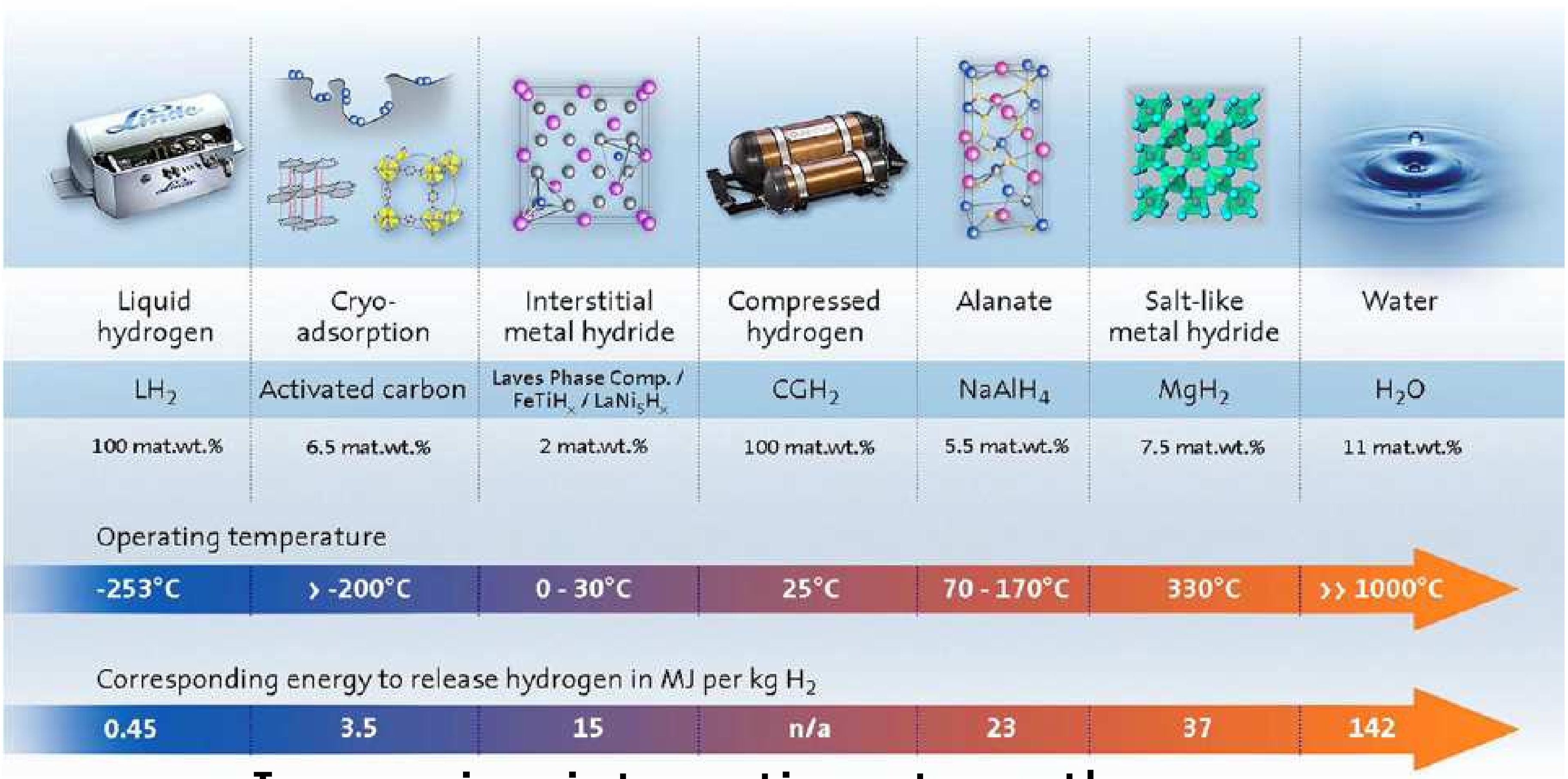
Hydrogen Storage inside materials

→ An interaction is needed to bind the H_2 or H inside the material. We will look into various interaction types with interactions ranging from weak to strong.



The interaction strengths have a direct effect on the operating conditions

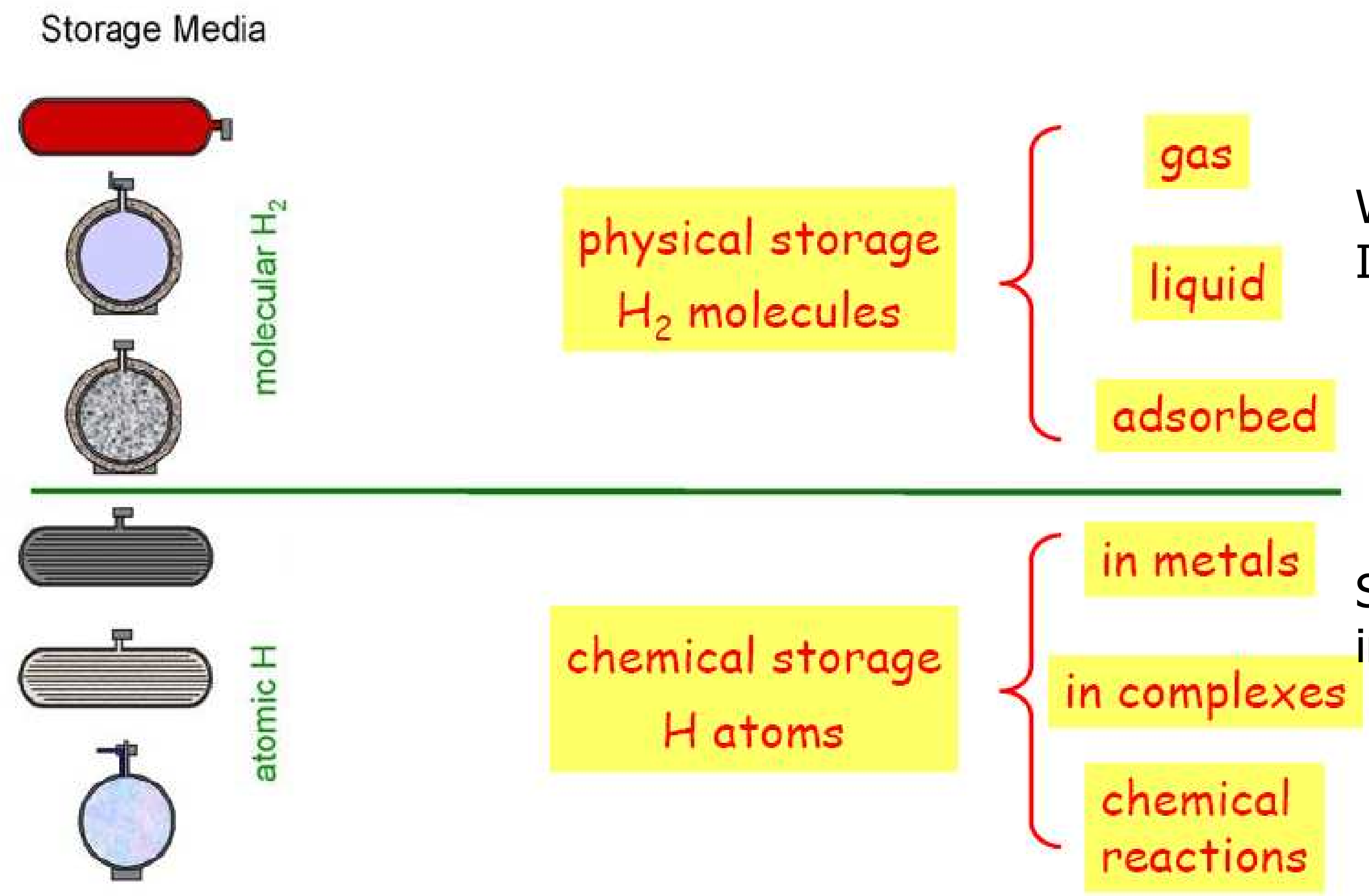
R. von Helmolt, U. Eberle / Journal of Power Sources 165 (2007) 833–843



	Liquid hydrogen	Cryo-adsorption	Interstitial metal hydride	Compressed hydrogen	Alanate	Salt-like metal hydride	Water
	LH_2	Activated carbon	Laves Phase Comp. / $FeTiH_x$ / $LaNi_5H_x$	CGH_2	$NaAlH_4$	MgH_2	H_2O
	100 mat.wt.%	6.5 mat.wt.%	2 mat.wt.%	100 mat.wt.%	5.5 mat.wt.%	7.5 mat.wt.%	11 mat.wt.%
Operating temperature	-253°C	> -200°C	0 - 30°C	25°C	70 - 170°C	330°C	>> 1000°C
Corresponding energy to release hydrogen in MJ per kg H_2	0.45	3.5	15	n/a	23	37	142

~Increasing interaction strength →

Stated otherwise: depending on the interactions the system stores H_2 or H:

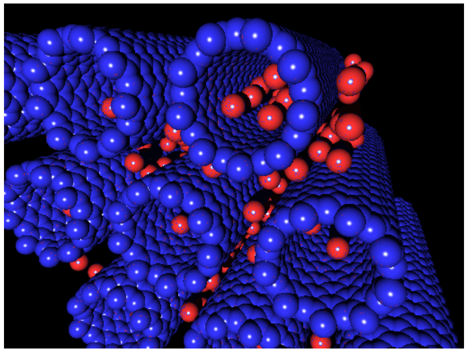


Weak
Interactions

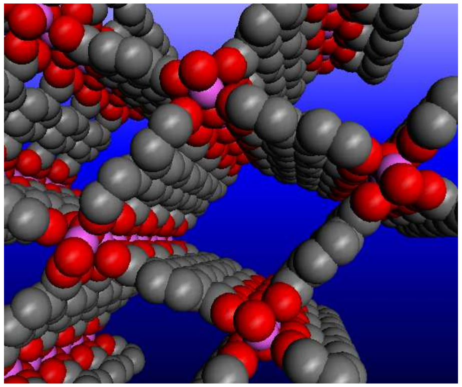
Strong
interactions

Starting from the weak interaction side: Hydrogen storage via surface adsorption

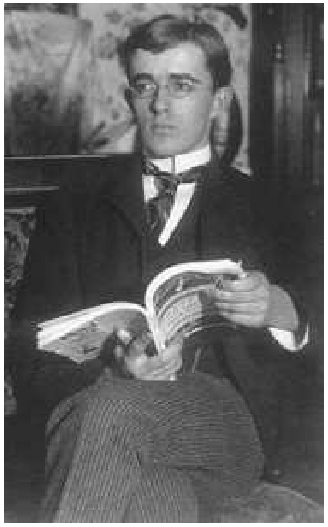
Nanocarbons



Metal organic frameworks



Hydrogen Storage using weak interactions: surface adsorption, physisorption
Gupta Chapter 12.



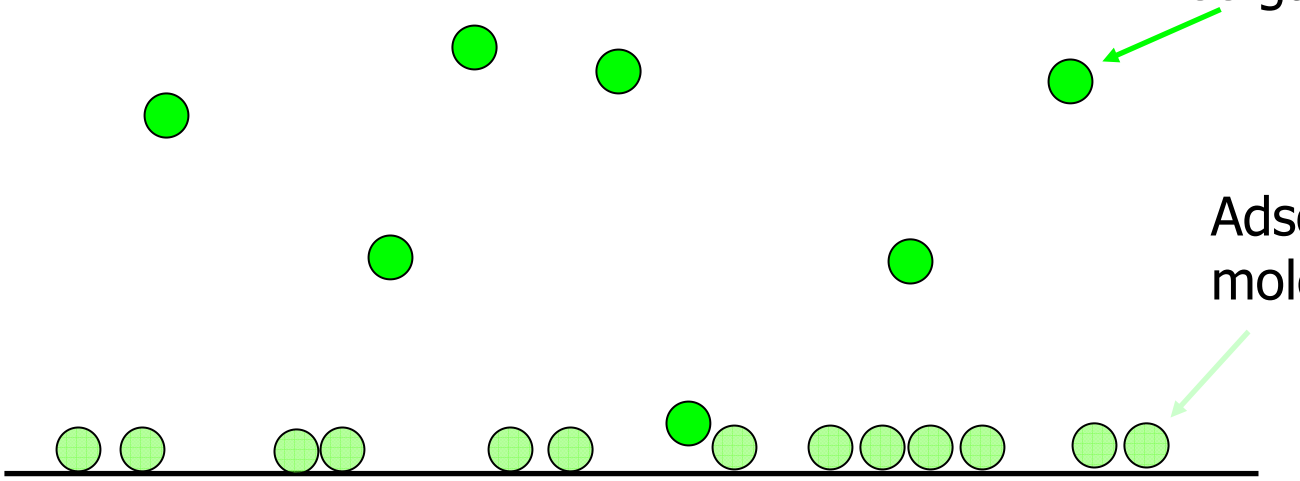
Irvin Langmuir
~ 1900

The Langmuir Isotherm

Whenever a gas is in contact with a solid there will be an equilibrium established between the molecules in the gas phase and the corresponding adsorbed species (molecules or atoms) which are bound to the surface of the solid.

Langmuir made significant advances in the fields of physics and chemistry and was in 1932 awarded the Nobel Prize for his work in surface chemistry.

Derivation Langmuir isotherm



Gas with the same temperature T

Free gas molecules

Adsorbed gas molecules

Surface with temperature T

- Assume that *n* molecules hit the surface per m^2 and per s.
- Assume that they stay on average a time τ bound at the surface
- Then there are on average σ molecules at the surface with

$$\sigma = n\,\tau$$

- Typically the residence time τ will be dependent on the adsorption interaction strength E_{ads}
- with increasing T the value of τ will go down as:

$$\tau = \tau_0 e^{\frac{E_{ads}}{k_B T}}$$

- If we now assume that there is a fixed, limited number of sites σ_0 available and a molecule only sticks to the surface when it hits a free site σ becomes:

$$\sigma = n\left(1-\frac{\sigma}{\sigma_0}\right)\tau \qquad \text{or} \qquad \sigma = \frac{\sigma_0 n\tau}{\sigma_0 + n\tau}$$

Where $\left(1-\frac{\sigma}{\sigma_0}\right)$ equals the chance to hit an empty spot on the surface.

- If we define $\theta = \frac{\sigma}{\sigma_0}$ as the 'surface coverage' we get:

$$\theta = \frac{n\tau}{\sigma_0 + n\tau} = \frac{\frac{n\tau}{\sigma_0}}{\left(1+\frac{n\tau}{\sigma_0}\right)}$$

It can be shown that $n = \frac{N_M P}{\sqrt{2\pi mRT}}$

So θ can be rewritten as: $\theta = \frac{\frac{n\tau}{\sigma_0}}{\left(1 + \frac{n\tau}{\sigma_0}\right)} = \frac{kP}{(1 + kP)}$

Where k is defined as:

$$k = \frac{N_M}{\sqrt{2\pi mRT}} \frac{\tau}{\sigma_0} = \frac{N_M}{\sqrt{2\pi mRT}} \frac{\tau_0}{\sigma_0} e^{\frac{E_{ads}}{k_B T}}$$

$$\theta = \frac{kP}{(1 + kP)}$$

describes the coverage θ as function of P at a constant T, and is called a Langmuir adsorption isotherm

Langmuir adsorption isotherms: used to measure adsorption energy

Also $kP = \frac{\theta}{(1-\theta)}$

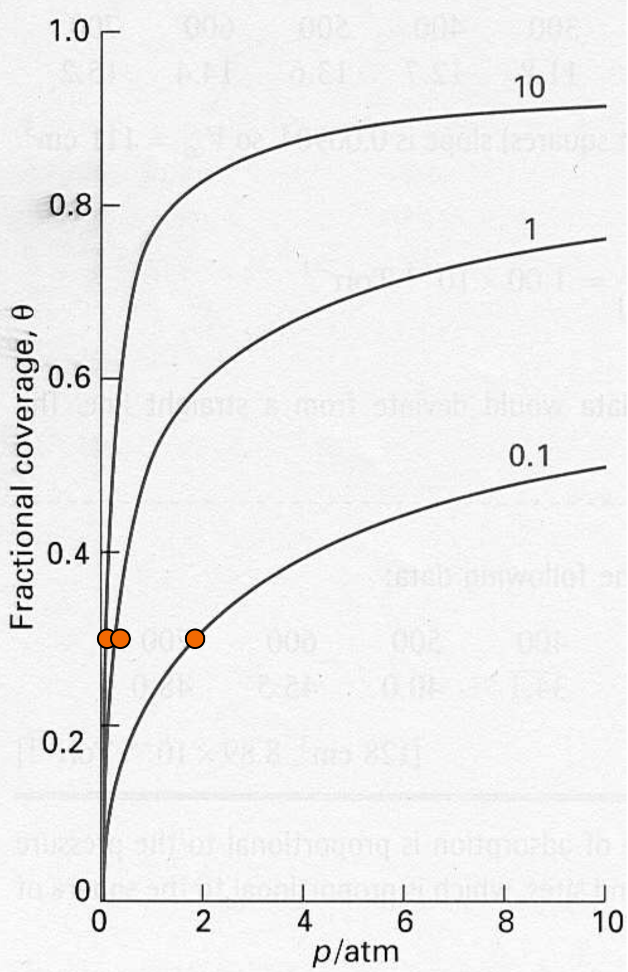
Therefore when θ is constant also $\ln k + \ln P = c$
with

$$\ln k = \ln\left(\frac{N_M}{\sqrt{2\pi mR}}\frac{\tau_0}{\sigma_0}\right) - \frac{1}{2}\ln T + \ln e^{\frac{E_{ads}}{k_B T}} = C - \frac{1}{2}\ln T + \frac{E_{ads}}{k_B T}$$

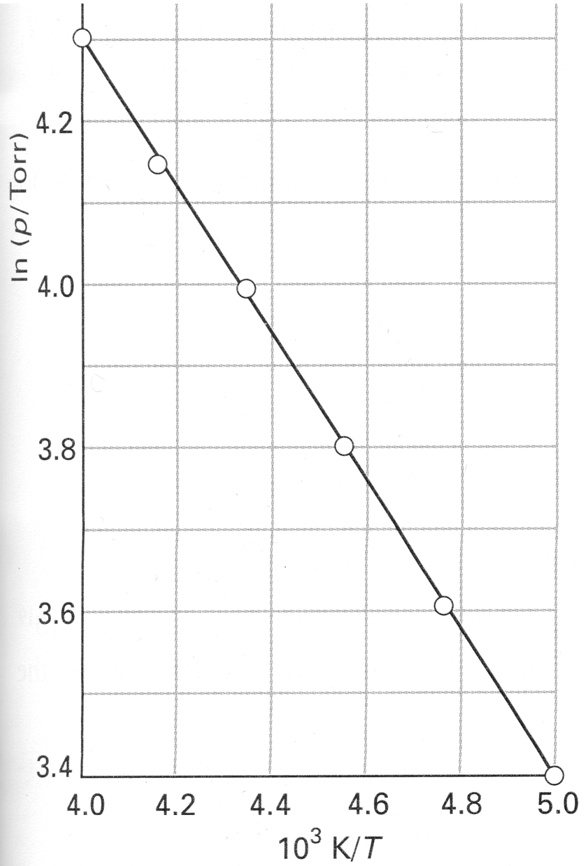
$$\left(\frac{\partial \ln P}{\partial T}\right)_\theta = -\left(\frac{\partial \ln k}{\partial T}\right)_\theta = \frac{1}{2T} + \frac{E_{ads}}{k_B T^2} \approx + \frac{E_{ads}}{k_B T^2}$$ for low T. With $$\frac{d\frac{1}{T}}{dT} = -\frac{1}{T^2}$$

$$\left(\frac{\partial \ln P}{\partial (1/T)}\right)_\theta = -\frac{E_{ads}}{k_B}$$

So from a graph of lnP at a constant coverage θ versus $1/T$ one obtains the adsorption energy E_{ads}



28.25 The Langmuir isotherm for non-dissociative adsorption for different values of K. so different T’s

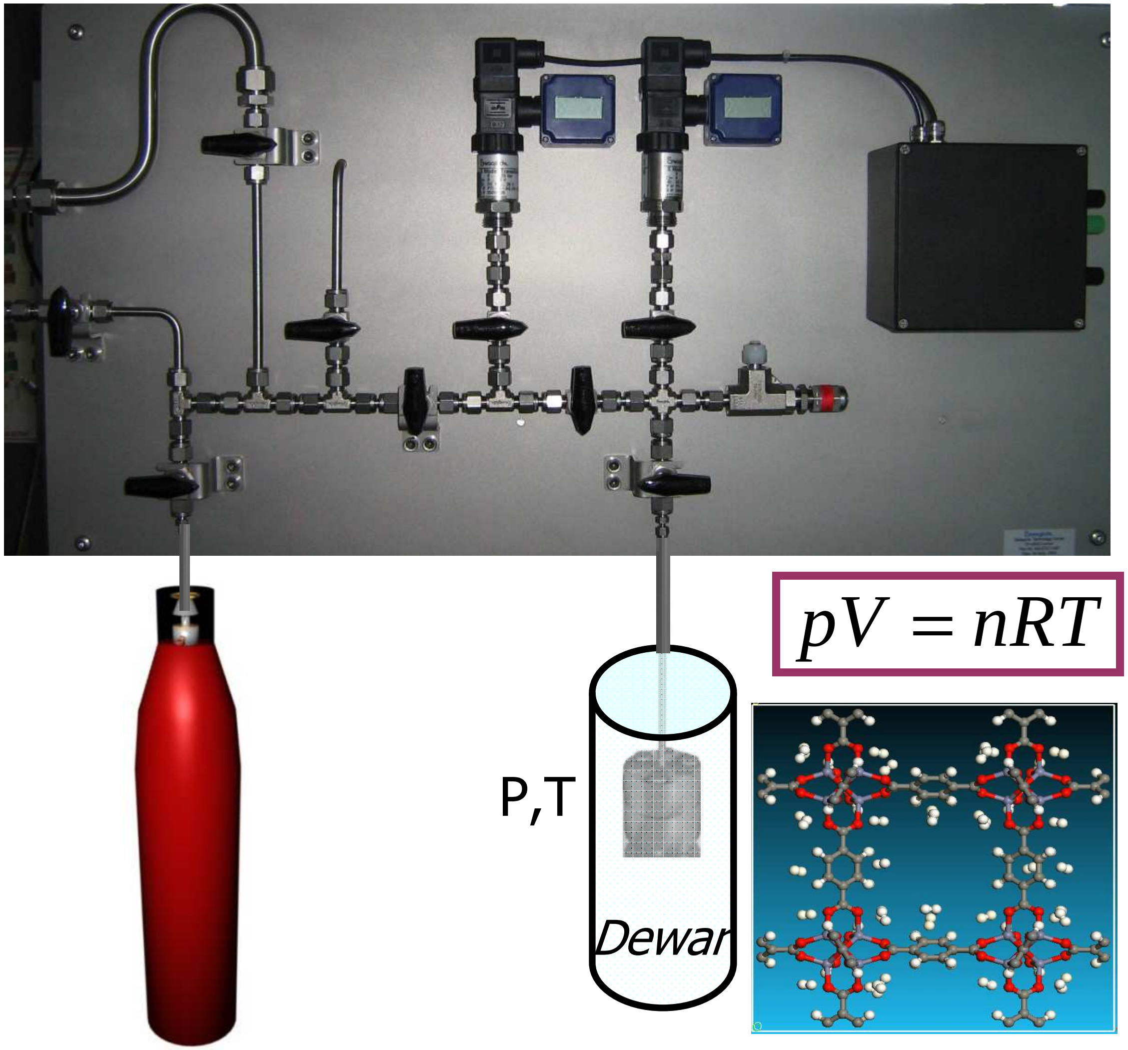


28.26 The isosteric enthalpy of adsorption can be obtained from the slope of the plot of $\ln p$ against $1/T$, where p is the pressure needed to achieve the specified surface coverage. The data used are from Example 28.2.

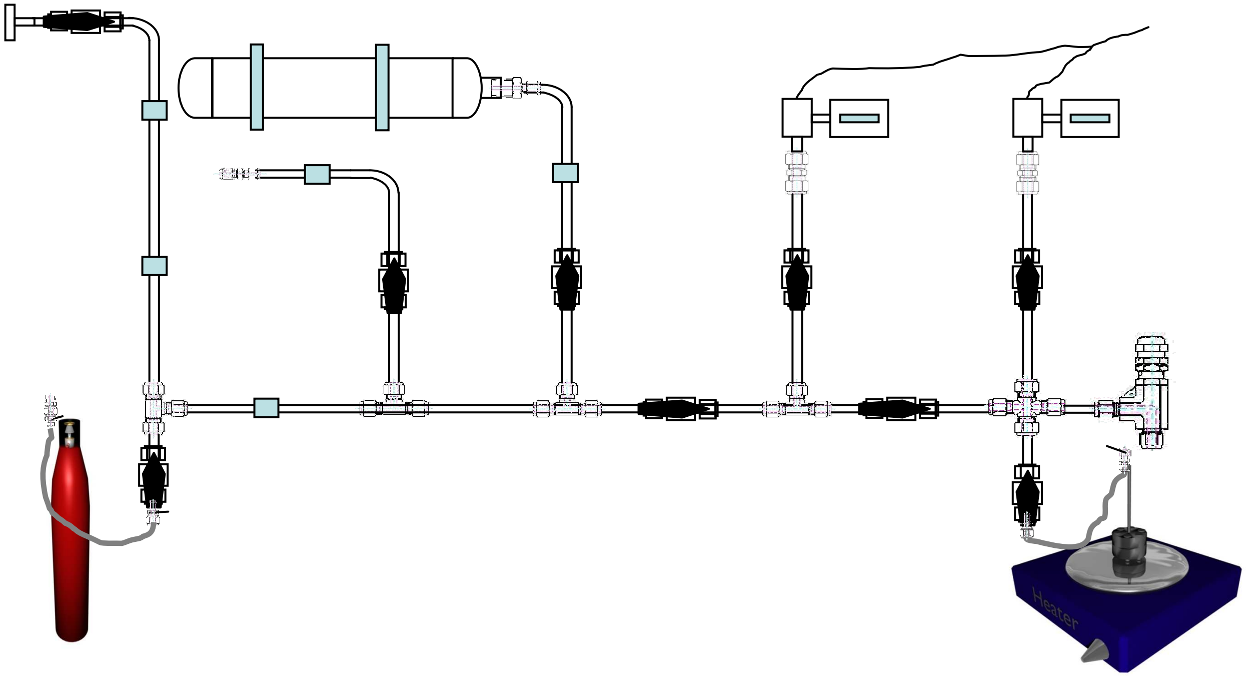
Which point is highest T?

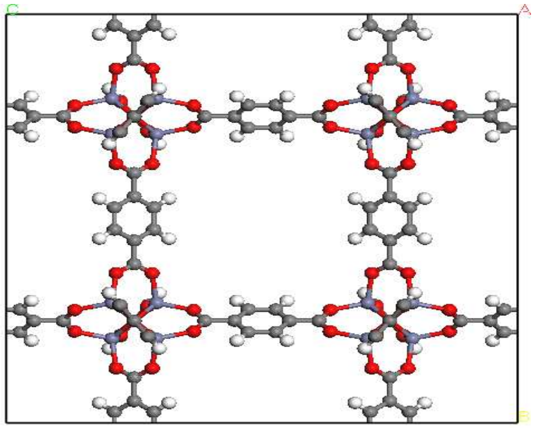
Left graph: most right point (has therefore lowest adsorption)
Right graph: most left point (needs therefore highest pressure to reach the same coverage)

Heat of Adsorption; measurement in the lab

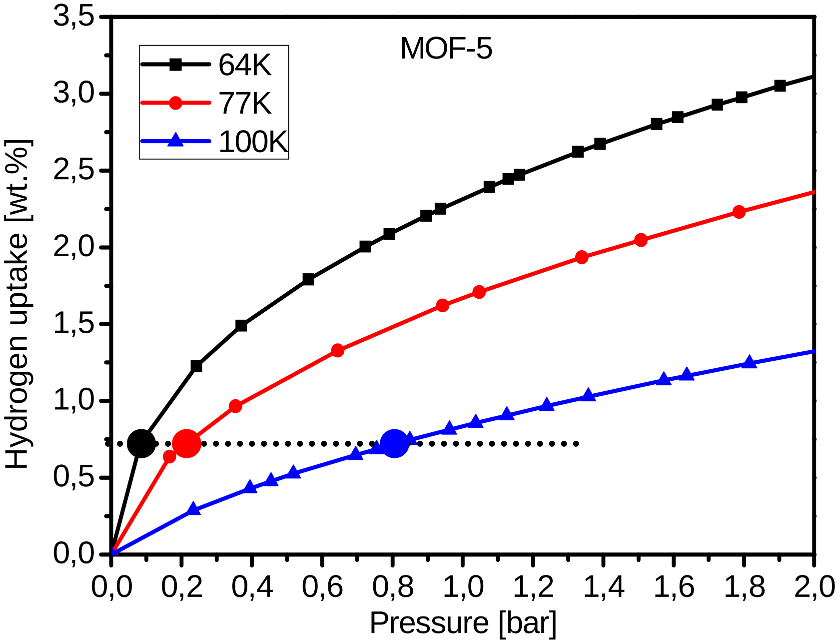


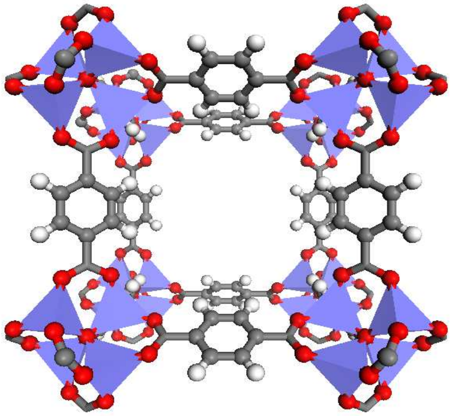
$$pV = nRT$$


Heater


C
A
B

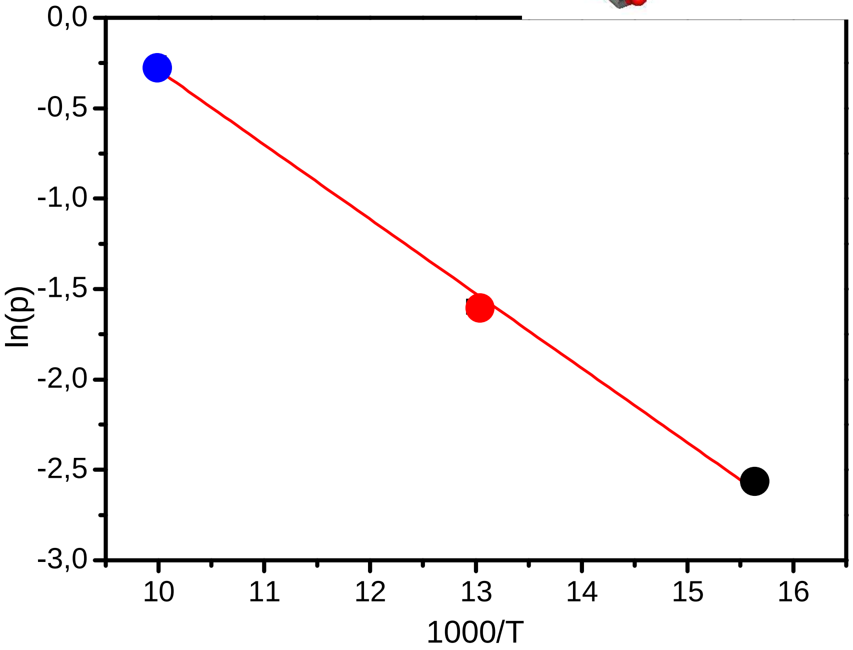
Heat of Adsorption





Clausius-Clapeyron equation:

$$\boxed{\left(\frac{\partial lnP}{\partial T}\right)_{\vartheta} = \frac{Q_{st}}{RT^{2}}}$$



At 0.7wt.% Q_{st}=3.42 kJ/mol H_2

Langmuir isotherm for dissociating gasses

- If gas A_2 dissociates upon adsorption, forming 2 A atoms, each of them needs to find an empty spot. Chance is proportional to $k_a PN(1-\theta)^2$.
- Likewise, chance for reassembling and desorption proportional to: $k_d(N\,\theta)^2$
  The sum leads to:

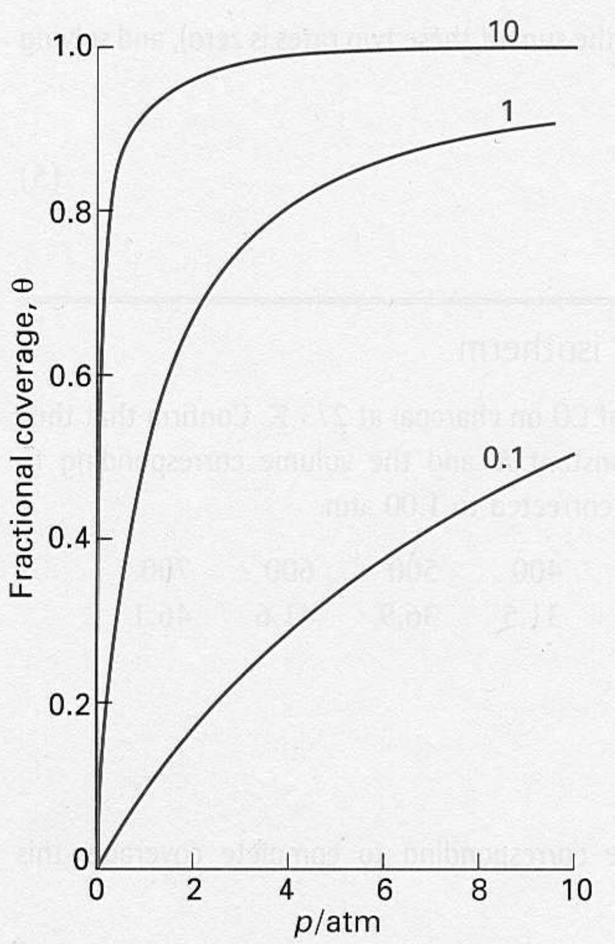
$$\frac{d\theta}{dt} = k_a P\{N(1-\theta)\}^2 - k_d(N\theta)^2$$

in equilibrium d θ/dt = 0 and its

solution is

$$\theta = \frac{(kp)^{\frac{1}{2}}}{1+(kp)^{\frac{1}{2}}}$$

With $k=k_a/k_d$



28.24 The Langmuir isotherm for dissociative adsorption ($X_2 \rightarrow 2X$) for different values of K.

In principle the shape of the isotherm could tell if a diatomic molecule like H_2 dissociates upon adsorption or not.

In practice H_2 only dissociates on certain catalyst surfaces like Pt.

It does not dissociate on for instance graphitic surfaces.

Additional monolayers adsorption: the BET isotherm

If the molecules adsorb in a monolayer only, we have the Langmuir isotherms. If on top of such monolayer additional monolayers can be adsorbed (before it becomes ordinary liquid) we come into the regime of the BET isotherm.

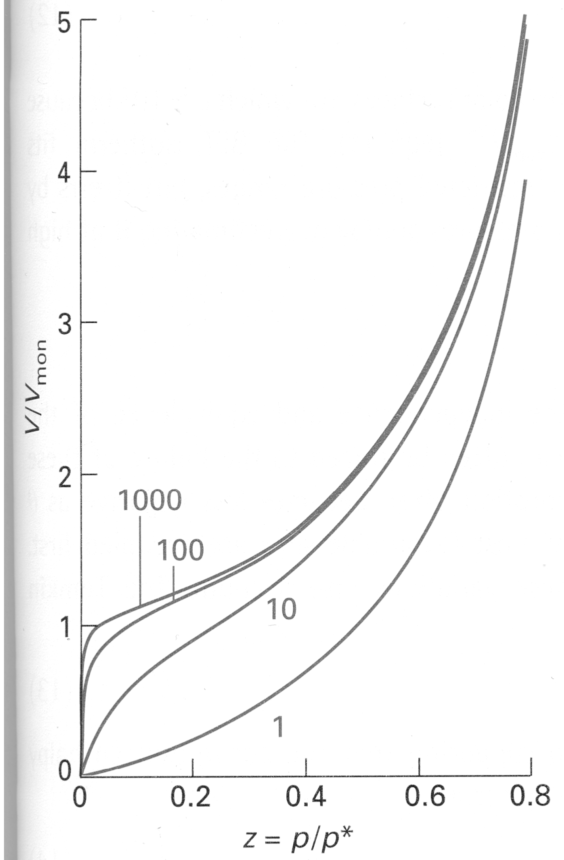
BET: Brunauer, Emmett, Teller

$$\frac{V}{V_{mon}} = \frac{cz}{\left((1-cz)(1-(1-c)z\right)}$$

With $z = P/P^*$ where P^* equals the vapour pressure of the liquefied gas at the same temperature.

$$c = e^{(E_{ads} - E_{vap})/kT}$$

Where $E_{ads} - E_{vap}$ is the difference between adsorption energy in the layer and the normal condensation energy in the liquid.



28.27 Plots of the BET isotherm for different values of c. The value of V/V_{mon} rises indefinitely because the adsorbate may condense on the covered substrate surface.

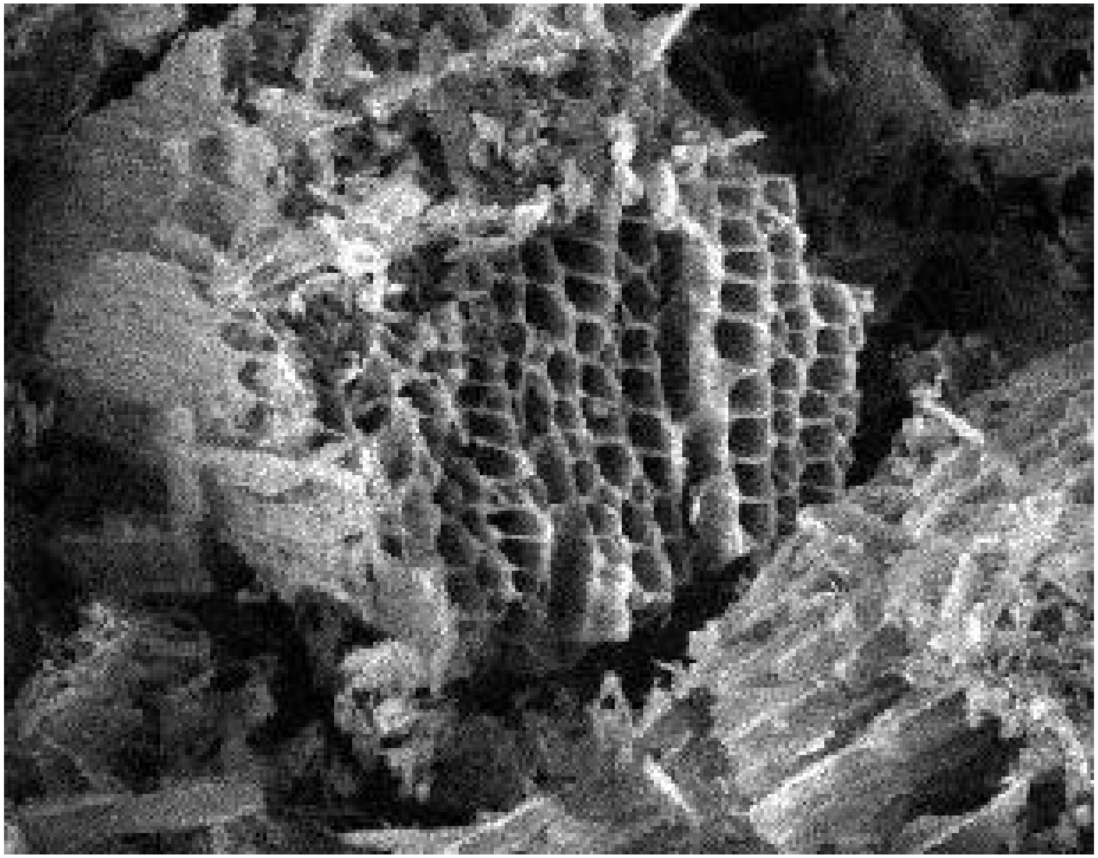
Additional monolayers adsorption:

Would you expect that to be relevant for hydrogen storage?

In principle not because: if one monolayer is present the second monolayer only feels H_2 molecules.
-the van der Waals interaction is that low between H_2 molecules that the boiling point is only 20 K at 1Bar…

We are now equipped to understand hydrogen storage via surface adsorption

Hydrogen storage in porous materials using surface adsorption
Also look into Gupta Ch 12



Warning: high storage of hydrogen in nanotubes appears false

~~Storage of hydrogen in single-walled carbon nanotubes,~~
~~Nature 386 (1997) 377,~~
~~Times Cited: 2473~~

~~Hydrogen storage in single-walled carbon nanotubes at room temperature,~~
~~Science 286 (1999) 1273.~~
~~Times Cited: 1278~~

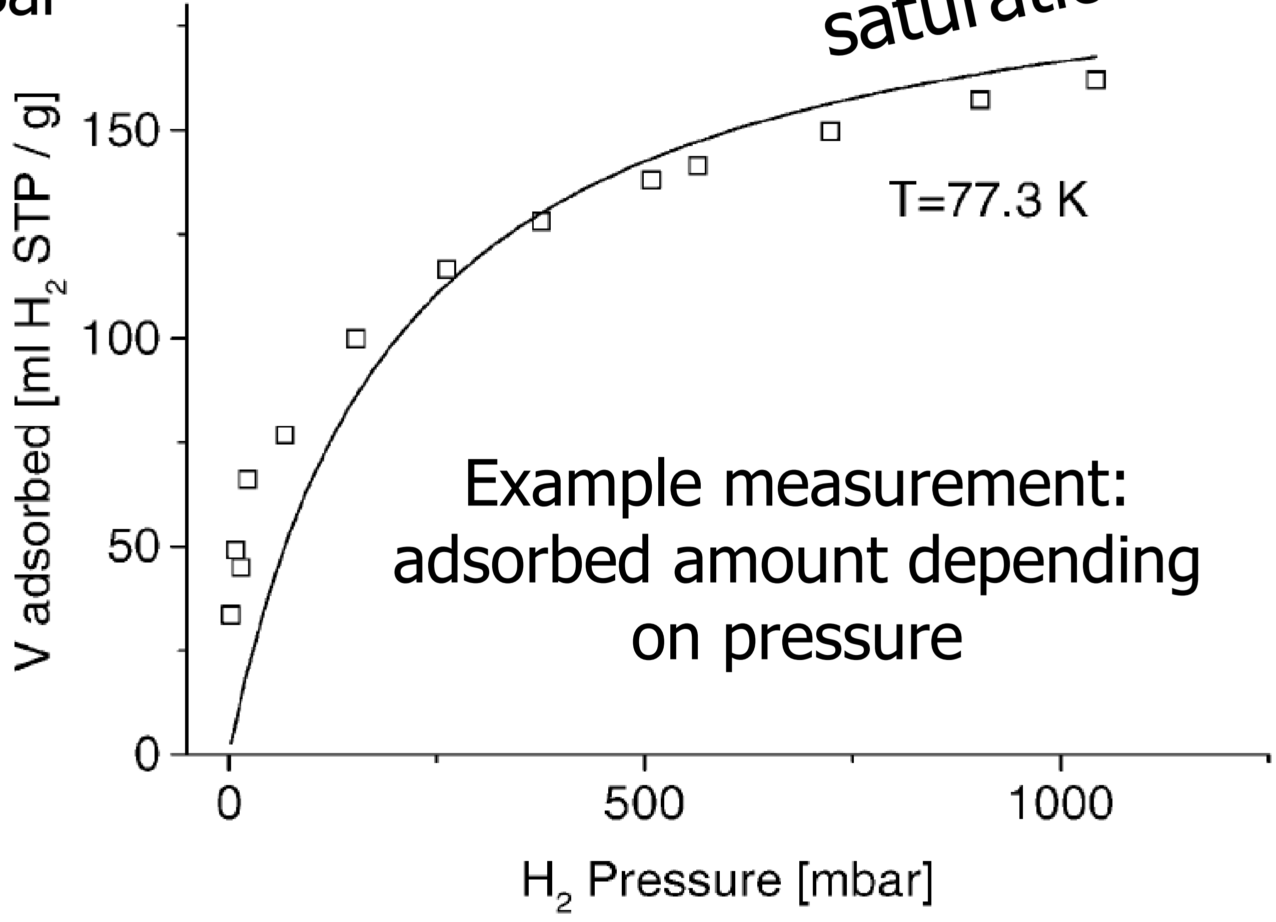
~~High H-2 uptake by alkali-doped carbon nanotubes under ambient pressure and moderate temperatures, Science 285 (1999) 91.~~
~~Times Cited: 801~~

Adsorption capacity of H_2 on nano carbons

Capacity: @ 77K & 2Bar

Nanotubes ~ 1 wt.%

Activated C ~ 2 wt.%



saturation

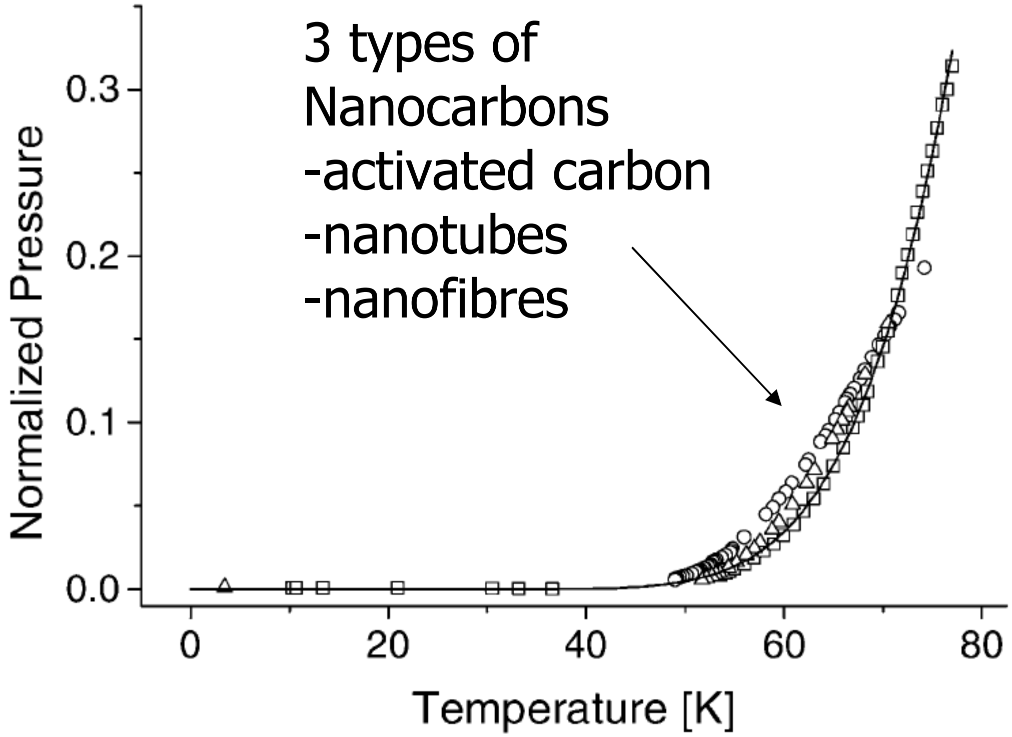
Example measurement: adsorbed amount depending on pressure

Nanotubes are not special, claims of storage of up to 20 wt.% are false…

Adsorption energy of H_2 on nano carbons

- The stronger the adsorption interaction, the higher the temperature is at which H_2 is released from the surface. From the hydrogen pressure above the sample an adsorption energy can be estimated of ~560K for all types of carbon.

→ nanotubes do not adsorb hydrogen any better than other carbons

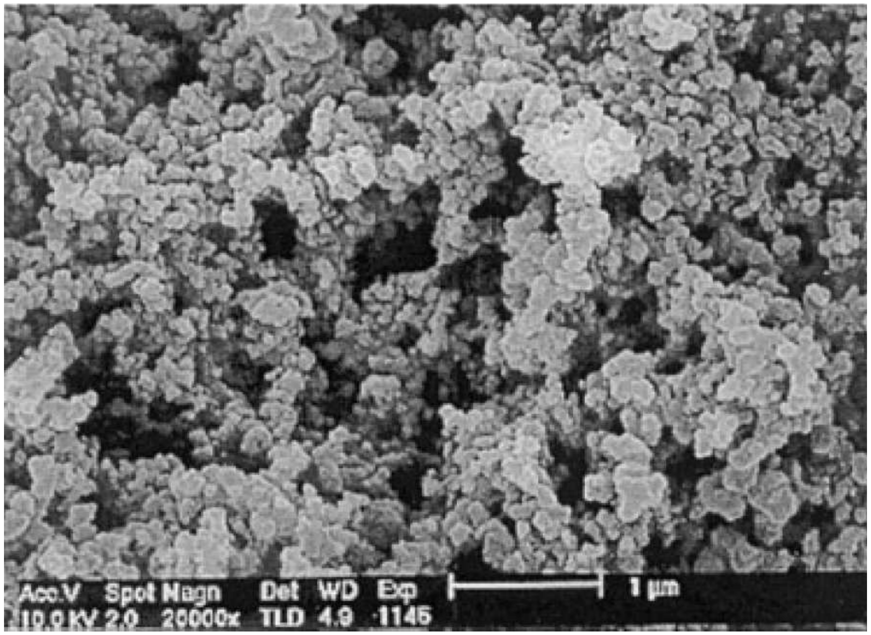


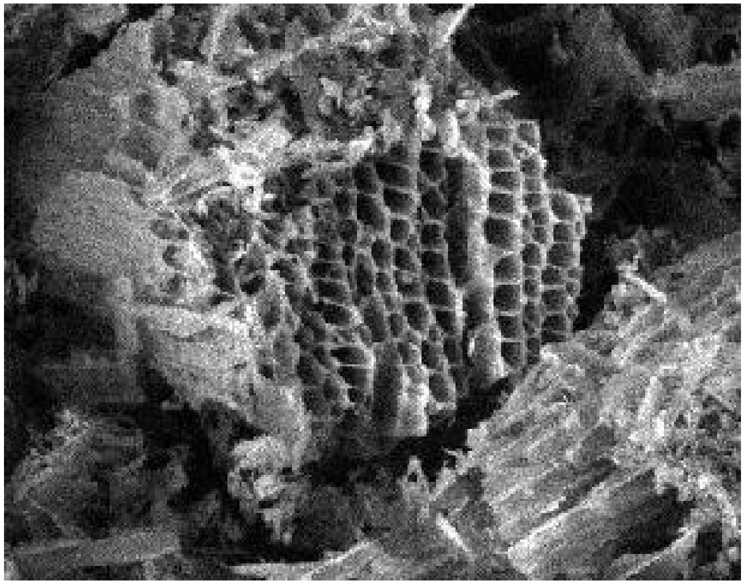
3 types of
Nanocarbons
-activated carbon
-nanotubes
-nanofibres

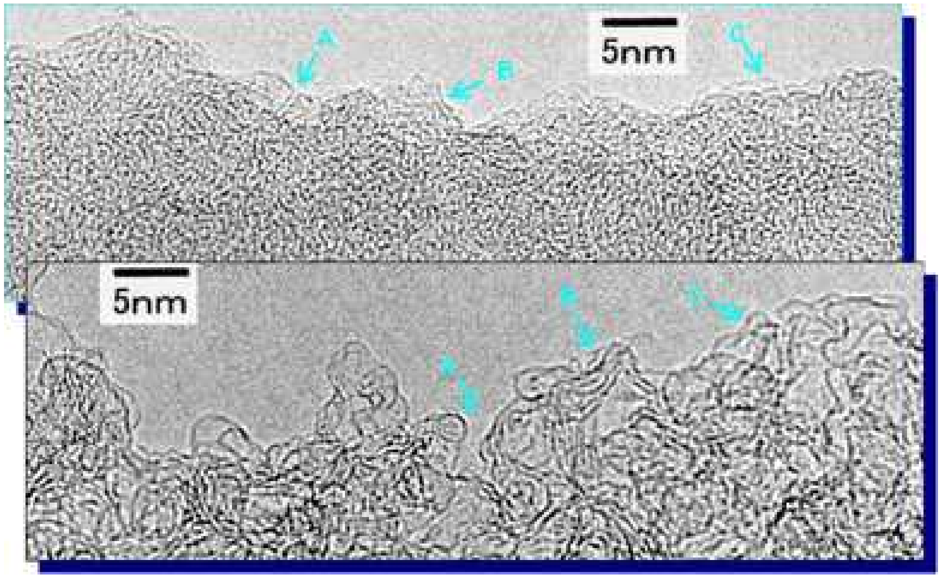
Schimmel et al. Chem Eur J 9 (2003) 4764

Activated carbons

Production by pyrolysis of organic materials or artificial nanostructured polymers

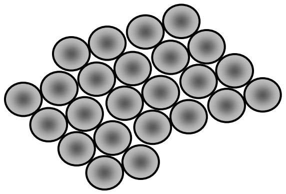






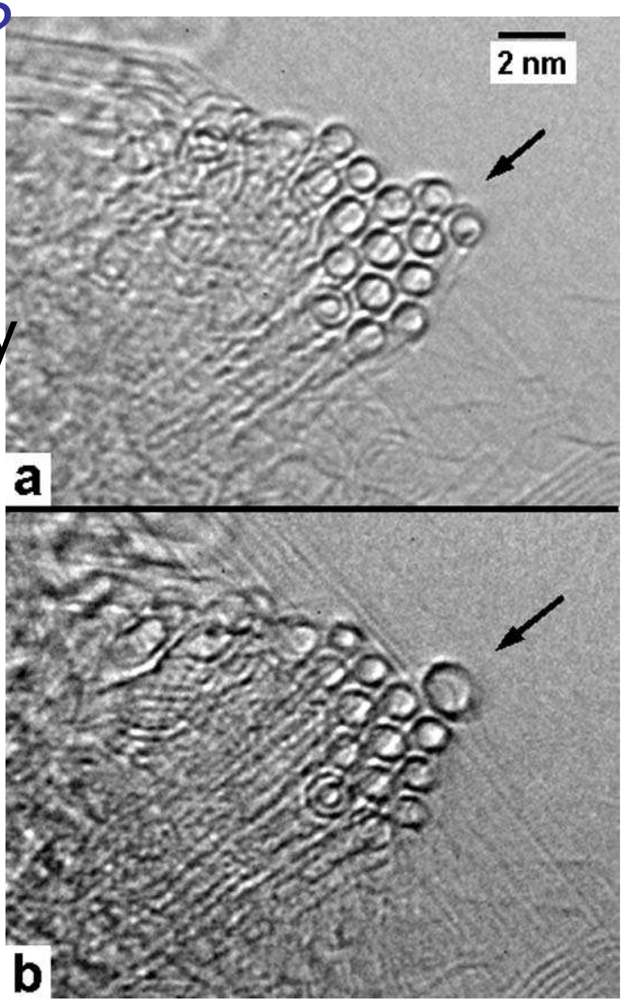
Why is there only low adsorption in nanotubes while you would expect a large surface to be available?

- they spontaneously form bundles which makes the surface area small
- when opened they can spontaneously close again, they can even coalesce, forming larger tubes



Only outer Surface accessible

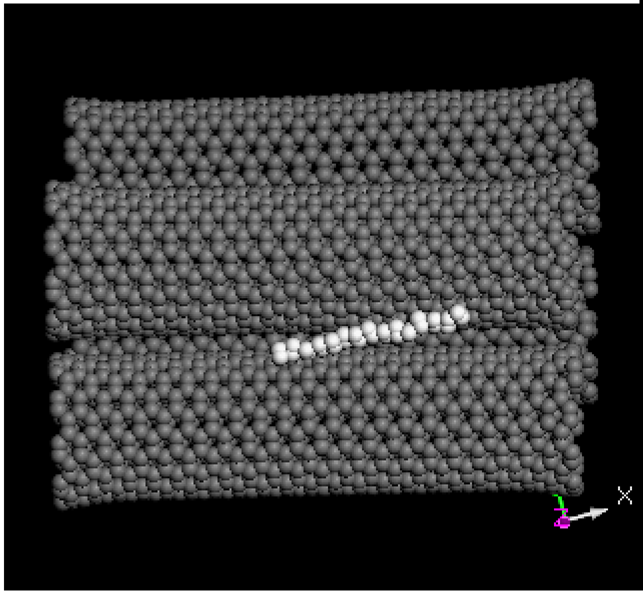
Annealing and welding during electron irradiation in electron microscope



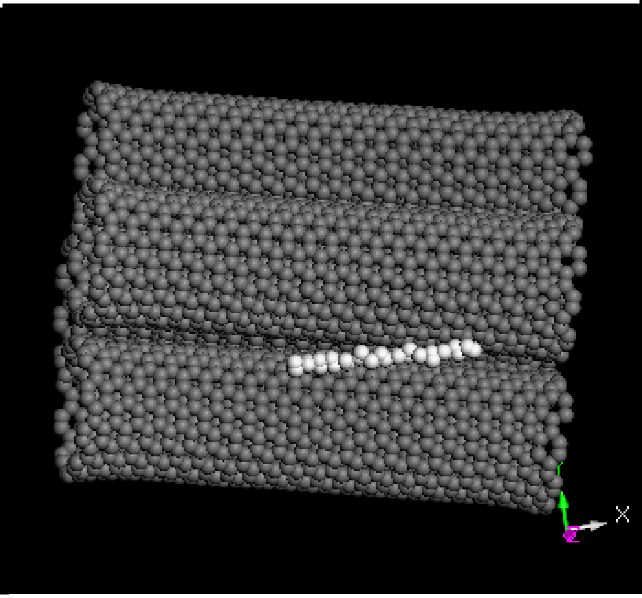
Science 288, 1226-1229 (2000)

Molecular dynamics simulations

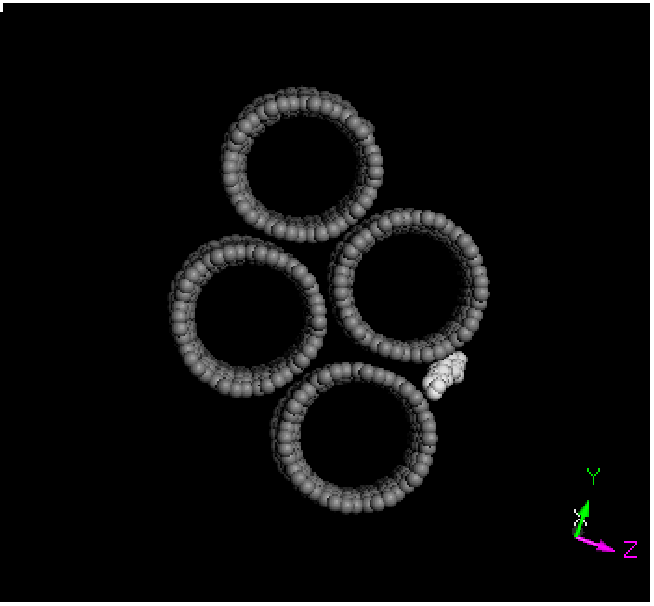
Modeling of molecular motions based on the physical interactions between atoms.



10K



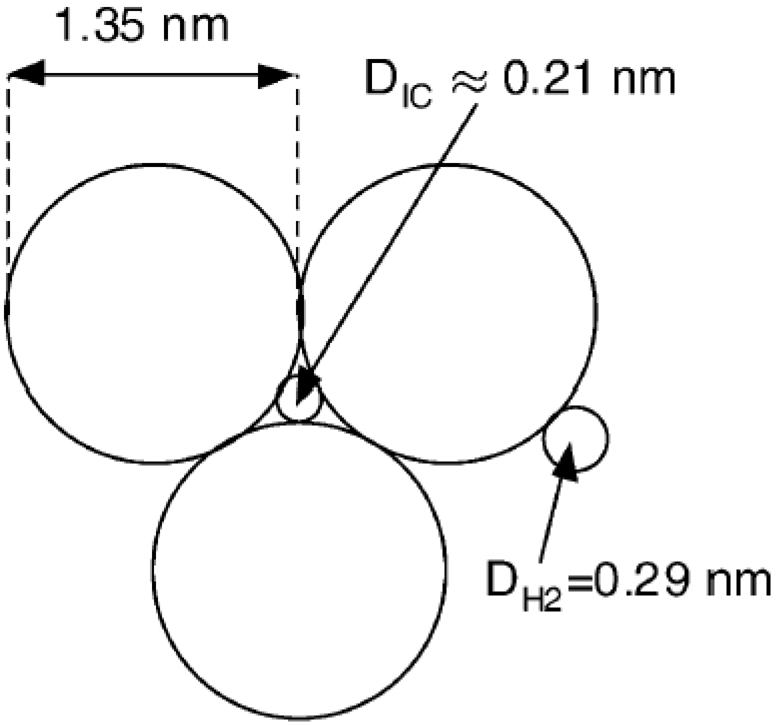
40K



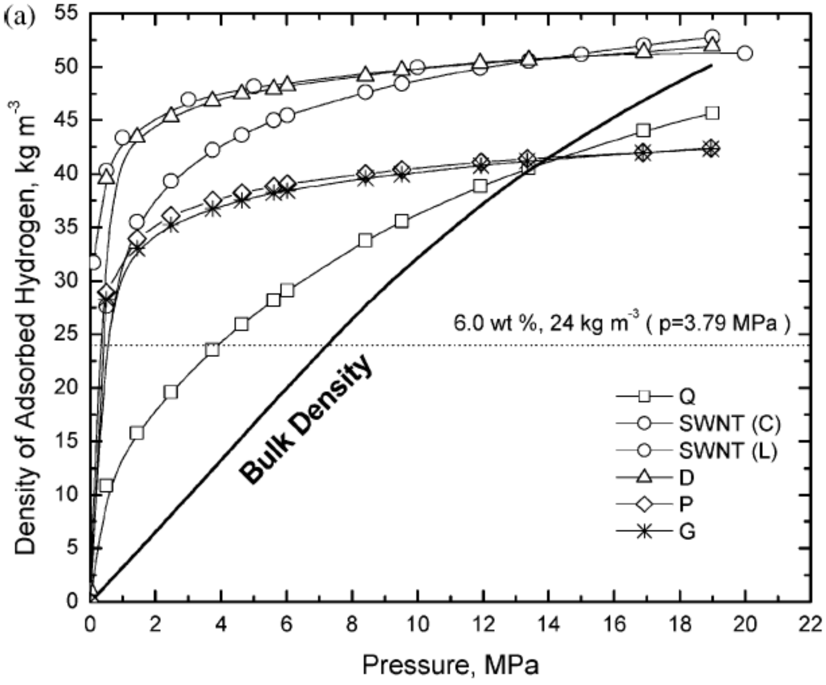
40K

Adsorption of H_2 in between tubes?

No: tubes leave apparently too little space in between the tubes.



The book (Gupta) presents theoretical simulations with very high storage capacities, based on idealized carbon structures.



Idealized carbon structures:

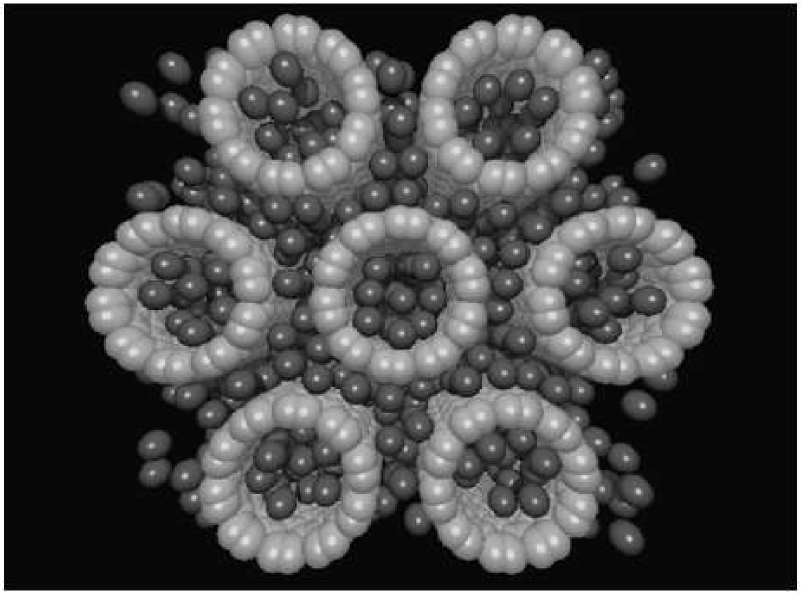
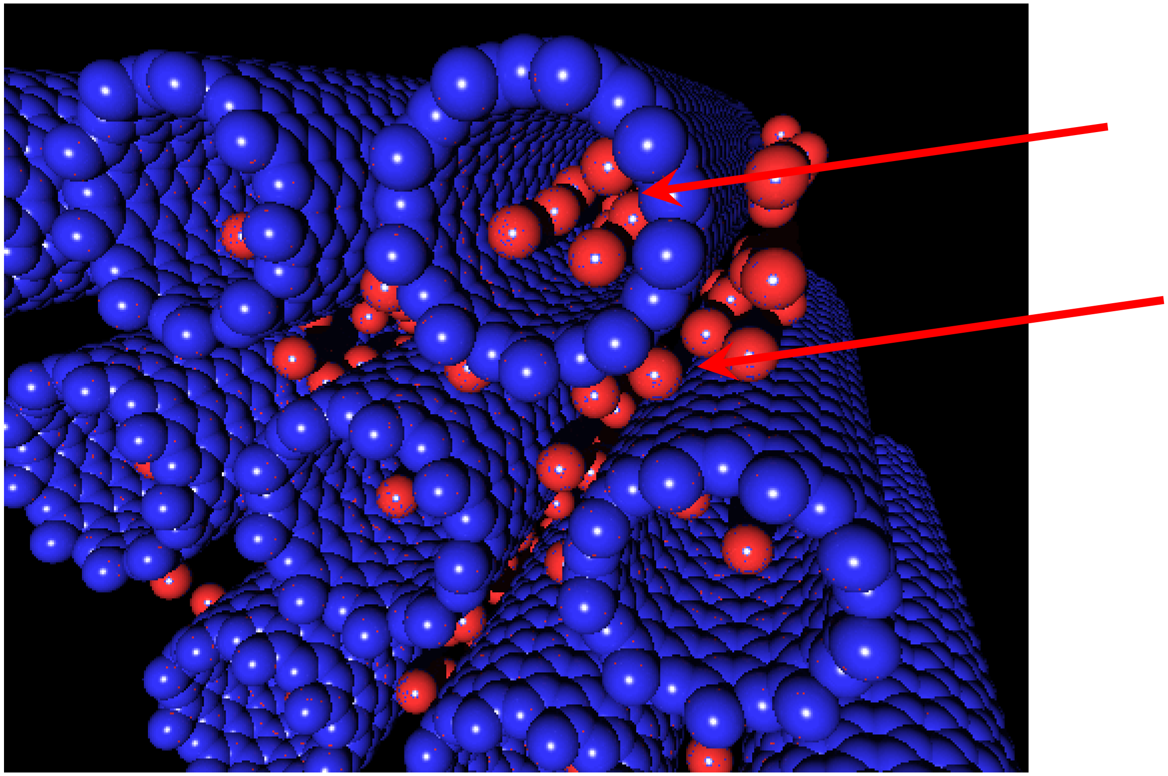


Fig. 3 A snapshot of hydrogen adsorbed in the idealized hexagonal bundle of the (10,10) carbon nanotubes at 3.8 MPa and 77 K.

Book p 414, PhysChemChemPhys 9 (2007) 1786

Note, however: the idealized structures have not been realized in practice. This is because the carbon cannot be structured at will, nanotubes stick together without H_2 being able to get in between, etc.



Although it looks pretty this does not happen!

- No H_2 in between tubes
- No H2 inside the tubes

What went wrong with this nanotube research?

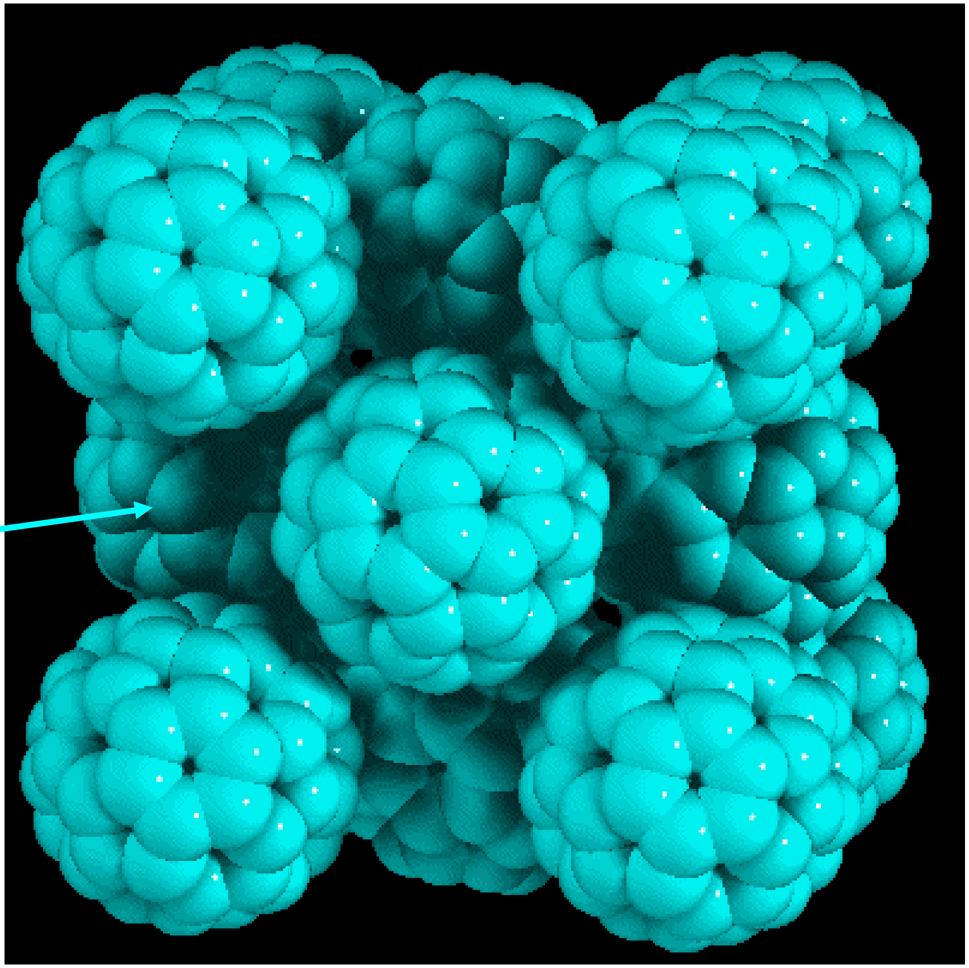
- detection of hydrogen: by weighing. This is not easy: all contaminants are heavier than H_2 and adsorbs much better e.g. water adsorbs well at RT on nanotubes and is 9 times heavier per molecule.

- assumption that nanotubes are very different from ‘ordinary’ nanostructured activated carbons

- contamination with some catalyst elements like Ti that store $H_{2,}$ so hydrogen was detected

- early nanotube samples contained mainly soot next to minority of tubes. All H_2 adsorption was attributed to few % tubes.

Another nano carbon: C_{60}



C_{60} FCC crystal

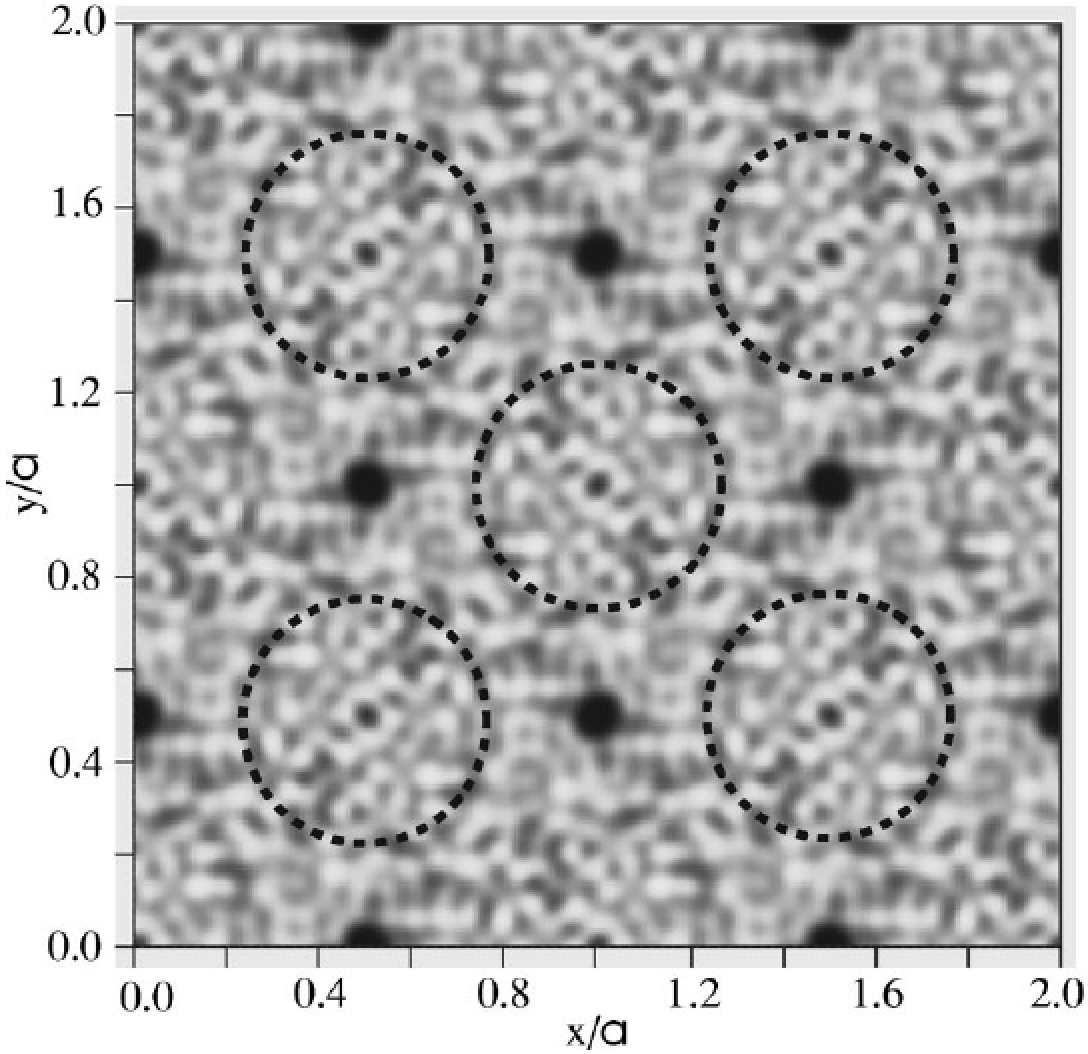
Large cavities

Adsorption of H_2 in between C_{60} Buckey balls?

Yes: one H_2 fits in certain pores in between C_{60}'s that have 0.41 nm diameter (so that tells you how much space is needed).

Resulting storage capacity: 1 H_2 on 60 C's

1/(1+60*12) gives low wt%…



Physical Review B 60 (1999) 6439.

Hydrogen storage capacity is proportional to surface area of the carbon materials.

This is at 77K, 1Bar

The specific surface area is usually determined by measuring the BET isotherm of nitrogen gas

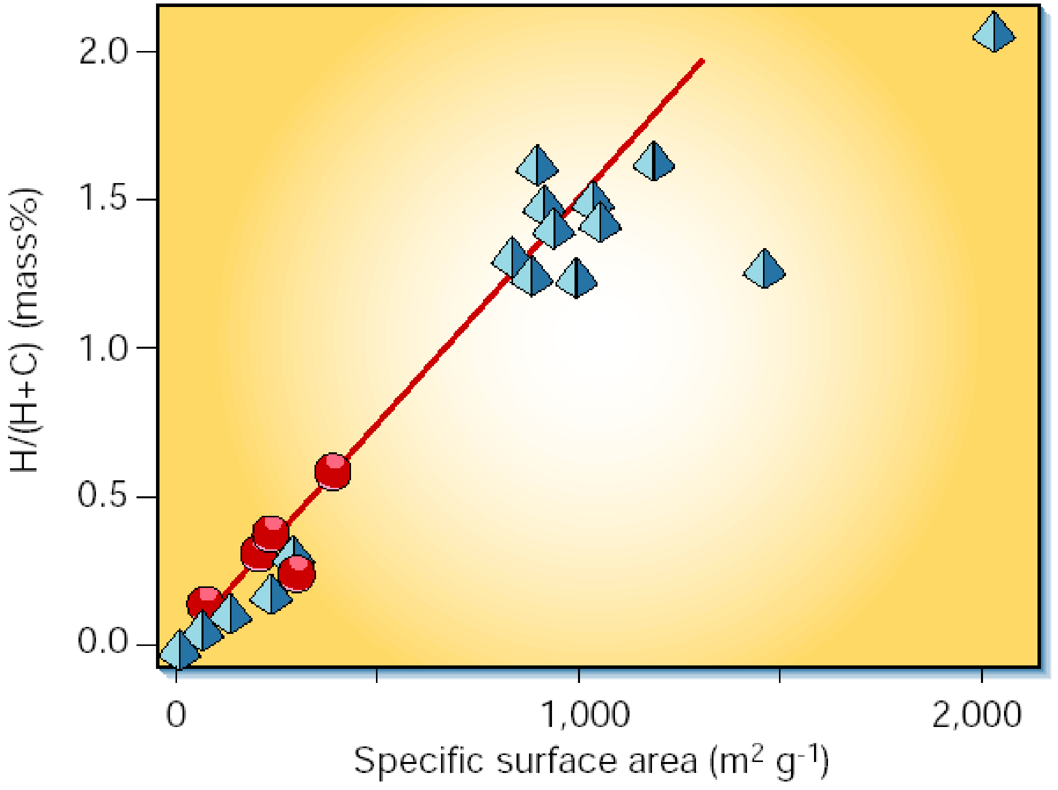
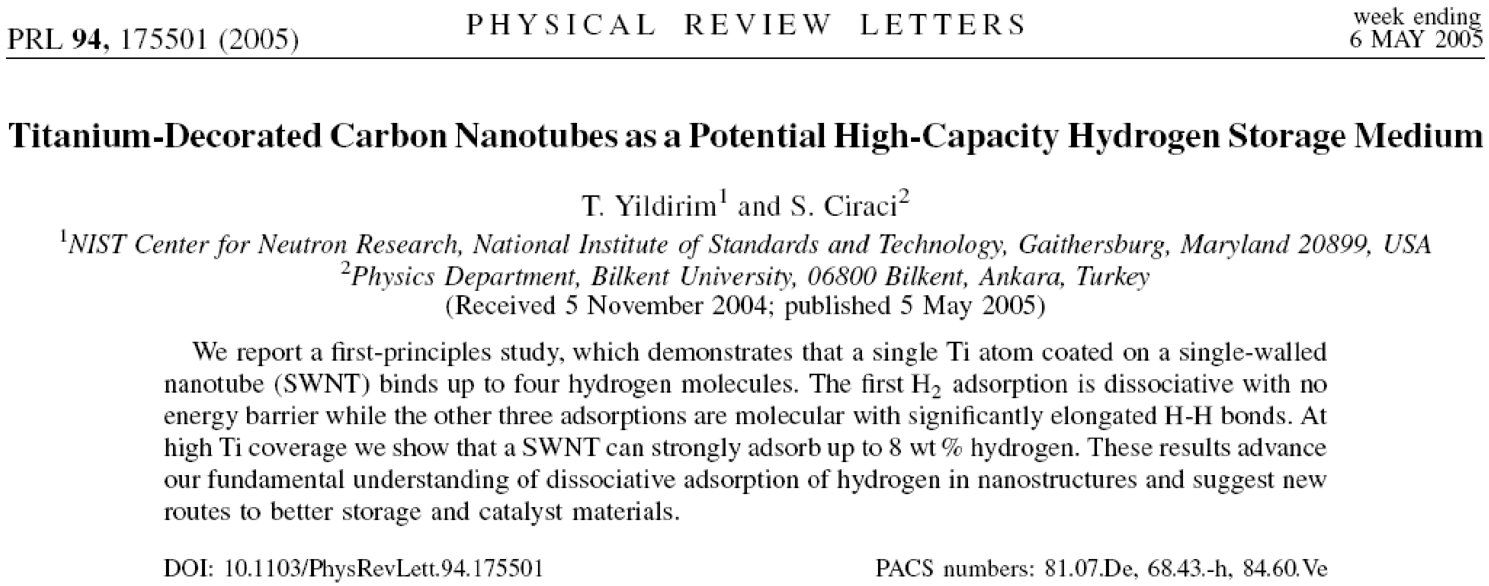


Figure 2 Reversibly stored amount of hydrogen on various carbon materials versus the specific surface area of the samples. Circles represent nanotube samples (best-fit line indicated), triangles represent other nanostructured carbon samples[17].

Schlapbach,Zuttel, Nature 414 (2001) 353.



PRL 94, 175501 (2005) PHYSICAL REVIEW LETTERS week ending 6 MAY 2005

Titanium-Decorated Carbon Nanotubes as a Potential High-Capacity Hydrogen Storage Medium

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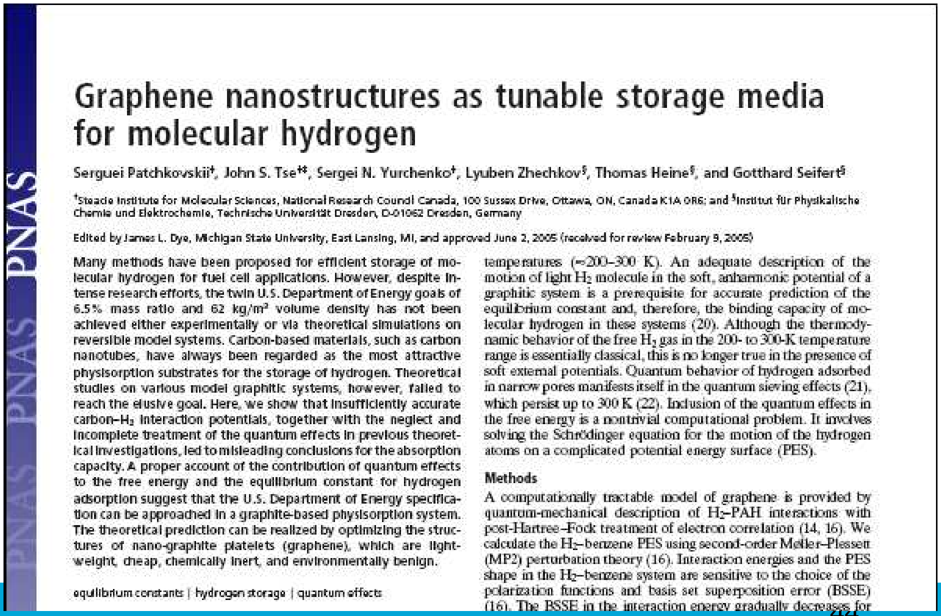
(Received 5 November 2004; published 5 May 2005)

We report a first-principles study, which demonstrates that a single Ti atom coated on a single-walled nanotube (SWNT) binds up to four hydrogen molecules. The first H_2 adsorption is dissociative with no energy barrier while the other three adsorptions are molecular with significantly elongated H-H bonds. At high Ti coverage we show that a SWNT can strongly adsorb up to 8 wt % hydrogen. These results advance our fundamental understanding of dissociative adsorption of hydrogen in nanostructures and suggest new routes to better storage and catalyst materials.

DOI: 10.1103/PhysRevLett.94.175501 PACS numbers: 81.07.De, 68.43.-h, 84.60.Ve

Still theoreticians proposed that hydrogen should stick to the carbon or modified titanium decorated carbon…



PNAS

Graphene nanostructures as tunable storage media for molecular hydrogen

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Edited by James L. Dye, Michigan State University, East Lansing, MI, and approved June 2, 2005 (received for review February 9, 2005)

Many methods have been proposed for efficient storage of molecular hydrogen for fuel cell applications. However, despite intense research efforts, the twin U.S. Department of Energy goals of 6.5% mass ratio and 62 kg/m^3 volume density has not been achieved either experimentally or via theoretical simulations on reversible model systems. Carbon-based materials, such as carbon nanotubes, have always been regarded as the most attractive physisorption substrates for the storage of hydrogen. Theoretical studies on various model graphitic systems, however, failed to reach the elusive goal. Here, we show that insufficiently accurate carbon–H_2 interaction potentials, together with the neglect and incomplete treatment of the quantum effects in previous theoretical investigations, led to misleading conclusions for the absorption capacity. A proper account of the contribution of quantum effects to the free energy and the equilibrium constant for hydrogen adsorption suggest that the U.S. Department of Energy specification can be approached in a graphite-based physisorption system. The theoretical prediction can be realized by optimizing the structures of nano-graphite platelets (graphene), which are lightweight, cheap, chemically inert, and environmentally benign.

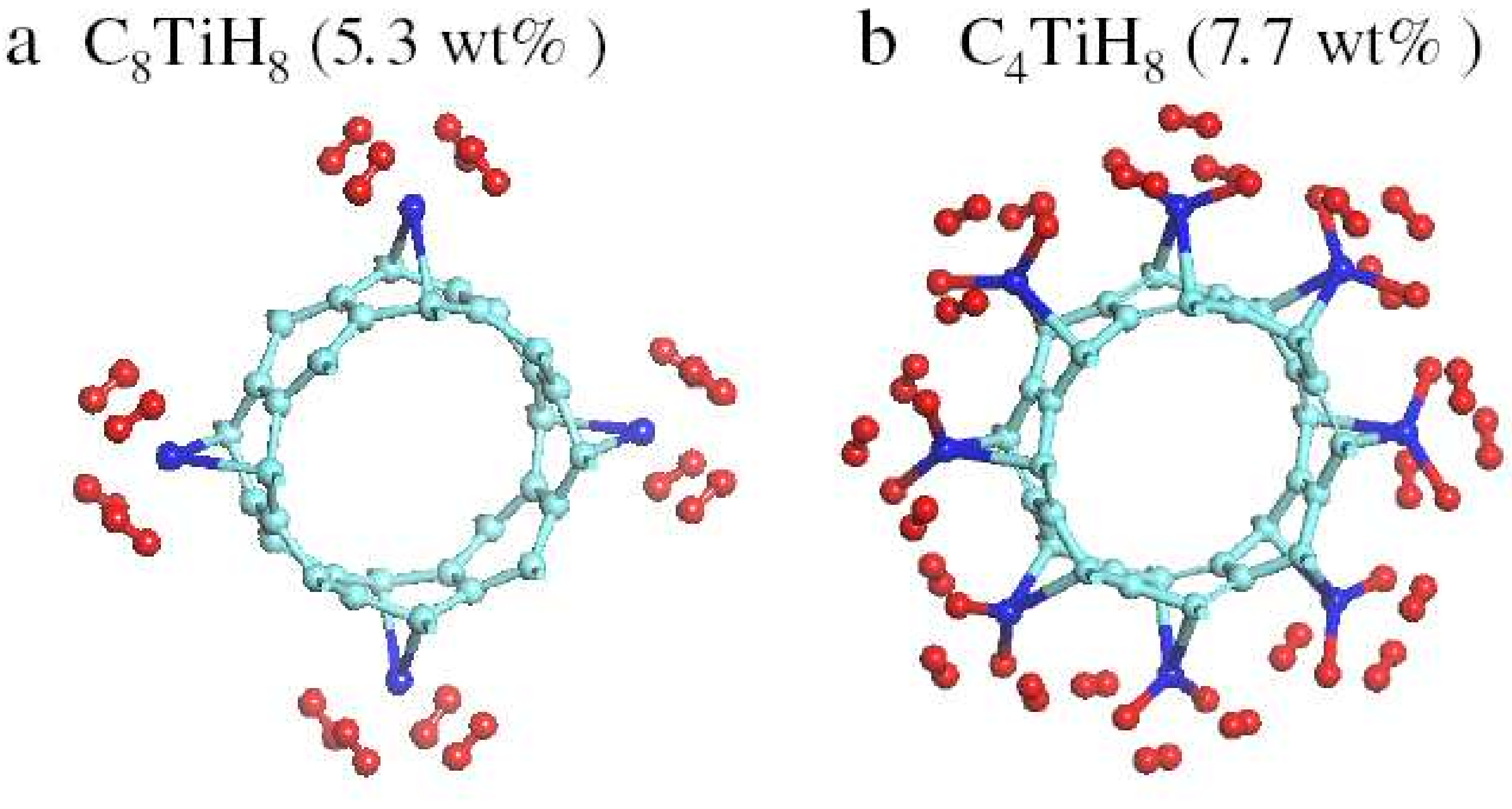
equilibrium constants | hydrogen storage | quantum effects

temperatures (≈200–300 K). An adequate description of the motion of light H_2 molecule in the soft, anharmonic potential of a graphitic system is a prerequisite for accurate prediction of the equilibrium constant and, therefore, the binding capacity of molecular hydrogen in these systems (20). Although the thermodynamic behavior of the free H_2 gas in the 200- to 300-K temperature range is essentially classical, this is no longer true in the presence of soft external potentials. Quantum behavior of hydrogen adsorbed in narrow pores manifests itself in the quantum sieving effects (21), which persist up to 300 K (22). Inclusion of the quantum effects in the free energy is a nontrivial computational problem. It involves solving the Schrödinger equation for the motion of the hydrogen atoms on a complicated potential energy surface (PES).

Methods

A computationally tractable model of graphene is provided by quantum-mechanical description of H_2–PAH interactions with post-Hartree–Fock treatment of electron correlation (14, 16). We calculate the H_2–benzene PES using second-order Møller–Plesset (MP2) perturbation theory (16). Interaction energies and the PES shape in the H_2–benzene system are sensitive to the choice of the polarization functions and basis set superposition error (BSSE) (16). The BSSE in the interaction energy gradually decreases for

Continued speculation (theory only): Ti decorated carbon nanotubes



a C_8TiH_8 (5.3 wt%)

b C_4TiH_8 (7.7 wt%)

FIG. 3 (color online). Two high-density hydrogen coverage on a Ti-coated (8, 0) nanotube.

Foreseeable problems with realizing such materials in practice:

- TiC is formed, not nanoporous and very stable
- Or Ti forms Ti metal particles, which leads to TiH_2 hydride

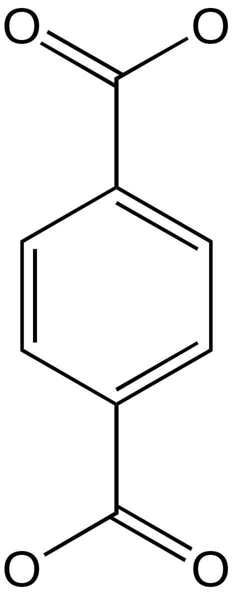
Conclusion nanocarbons:

- hydrogen storage occurs only at low temperatures because the adsorption interaction is ~ 550K or ~ 5 kJ/mol. Good for applications at low T only (<80K).

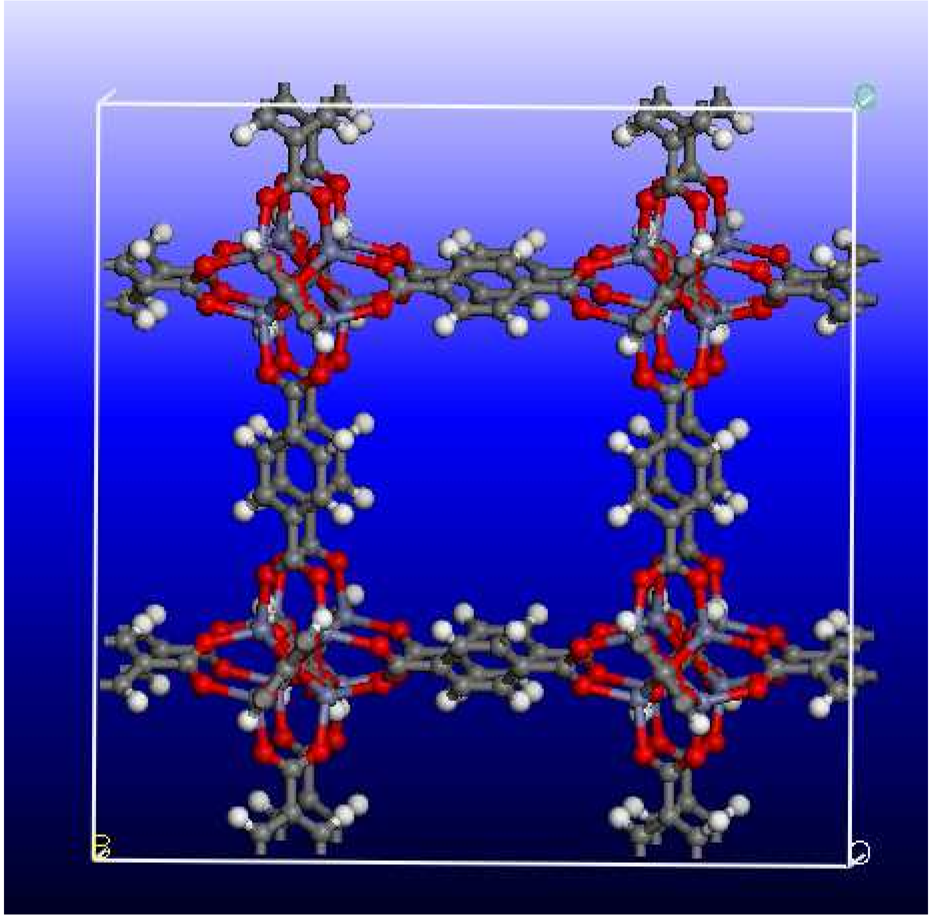
- The adsorption capacity is proportional to the accessible surface area of the nano materials. Because nanotubes form bundles they have lower surface area than the best activated carbons.

- Unfortunately researcher have reported record storage capacities based on experimental errors.

Metal Organic Frameworks MOFs: fully ordered crystalline nanoporous materials

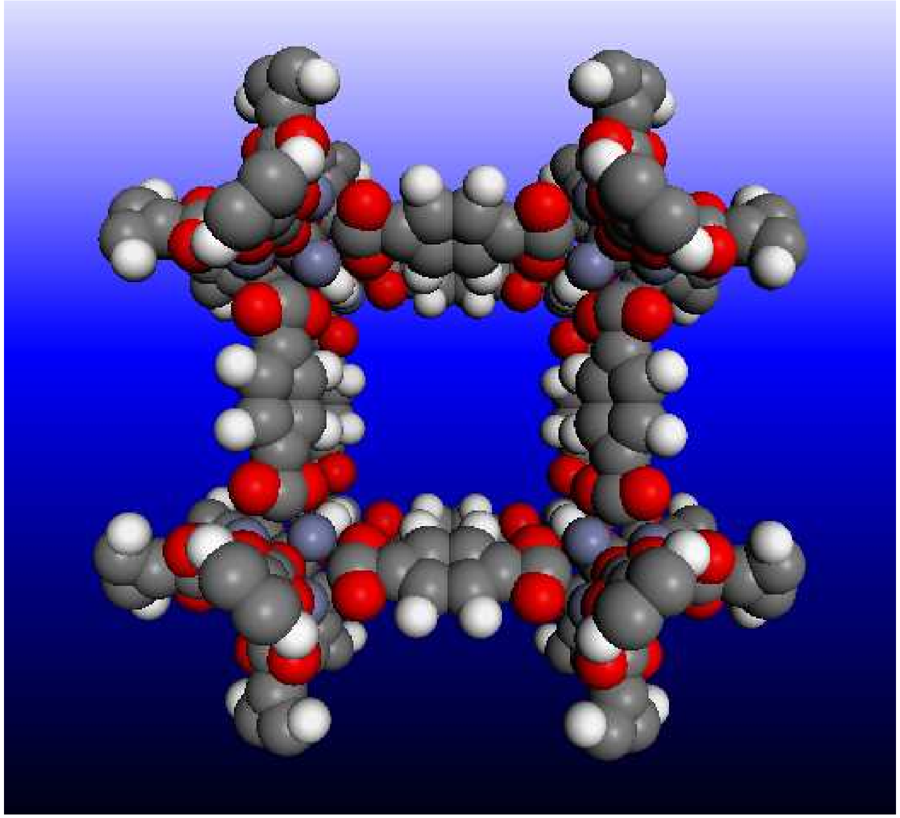


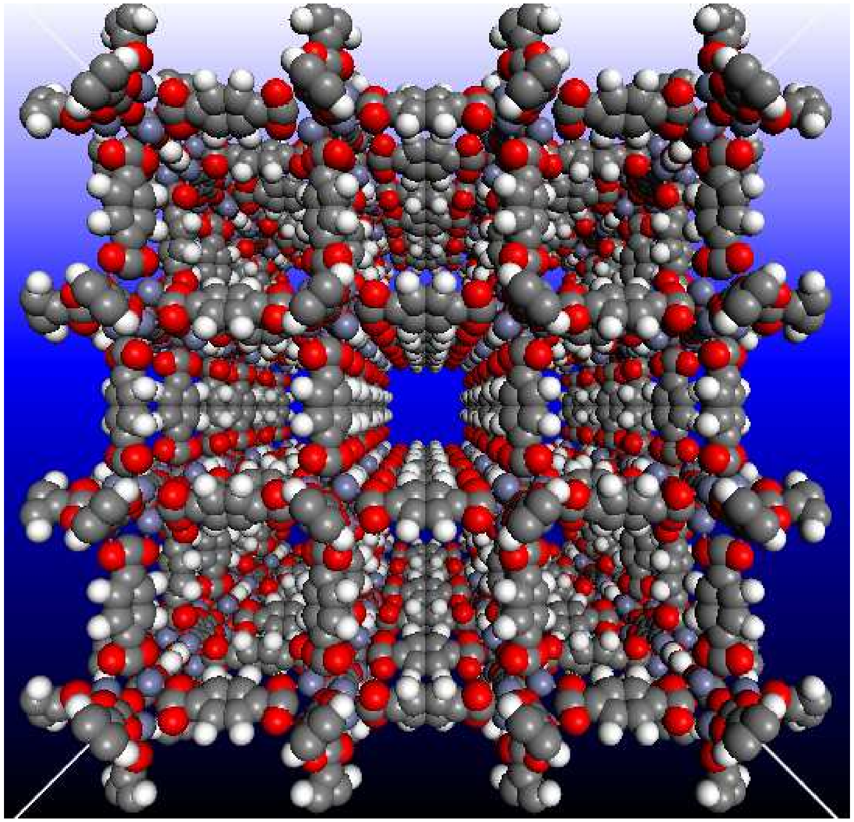
Terephthalic acid in MOF-5



“MOF-5”

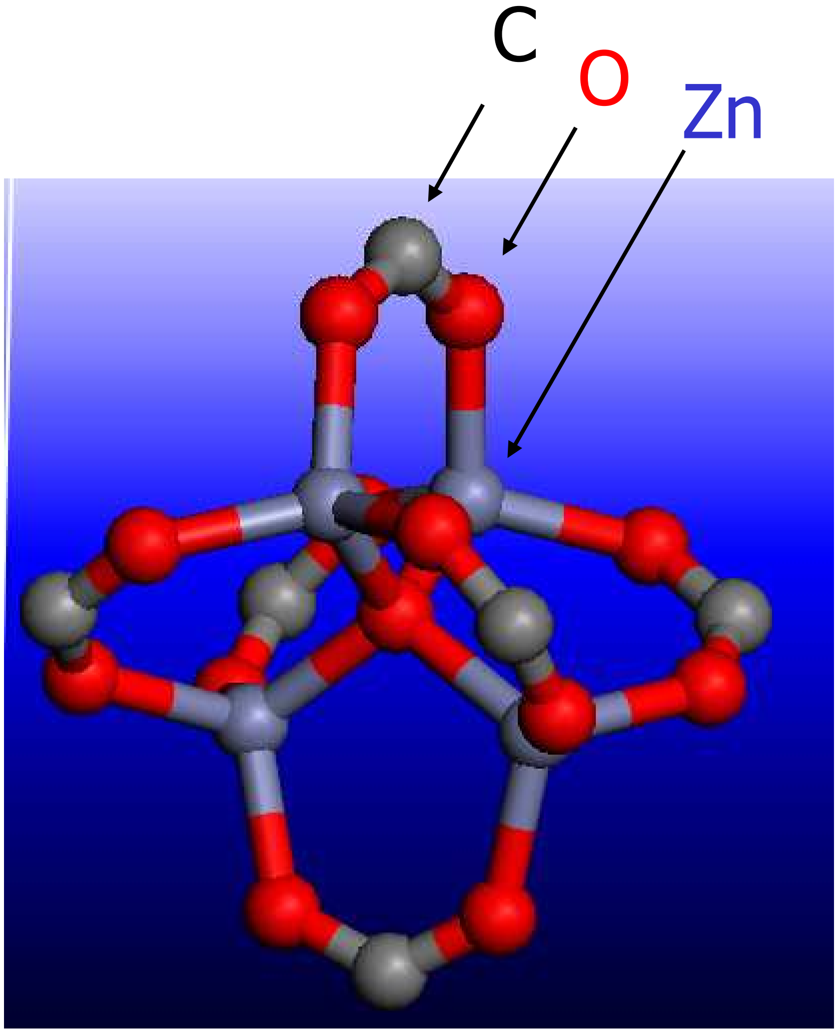
Highly porous Metal Organic Frameworks





MOF-5 Rosi et al, Science 2003

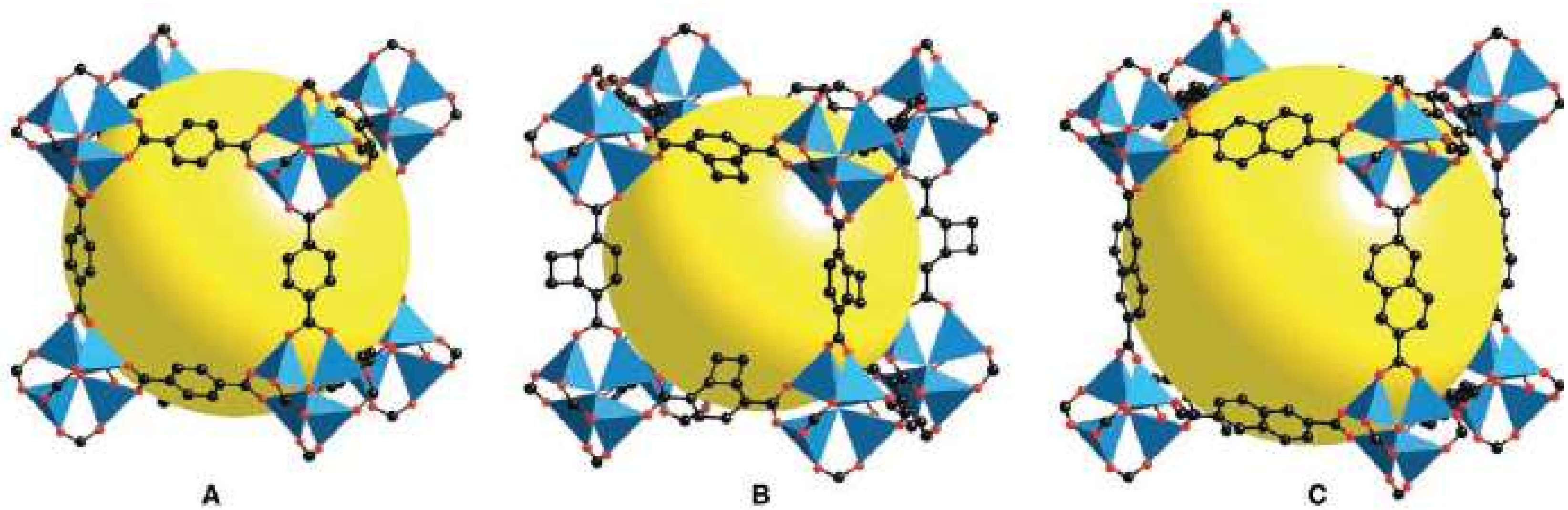
The COO groups form a cluster with 4 Zn ions and one central O atom



MOFs

- metal ion clusters bound by organic linker molecules with acid groups
- The framework is quite stable because of:
  - the preference for certain coordinations of the metal ions by O's
  - the rigidity of the linker molecules
- different organic linkers can be used, making the pores larger/smaller
- surface area's up to 4500 m^2g^{-1} are reported

  (larger than activated carbons max~2200 m^2g^{-1})



Science 300 (2003) 1127.

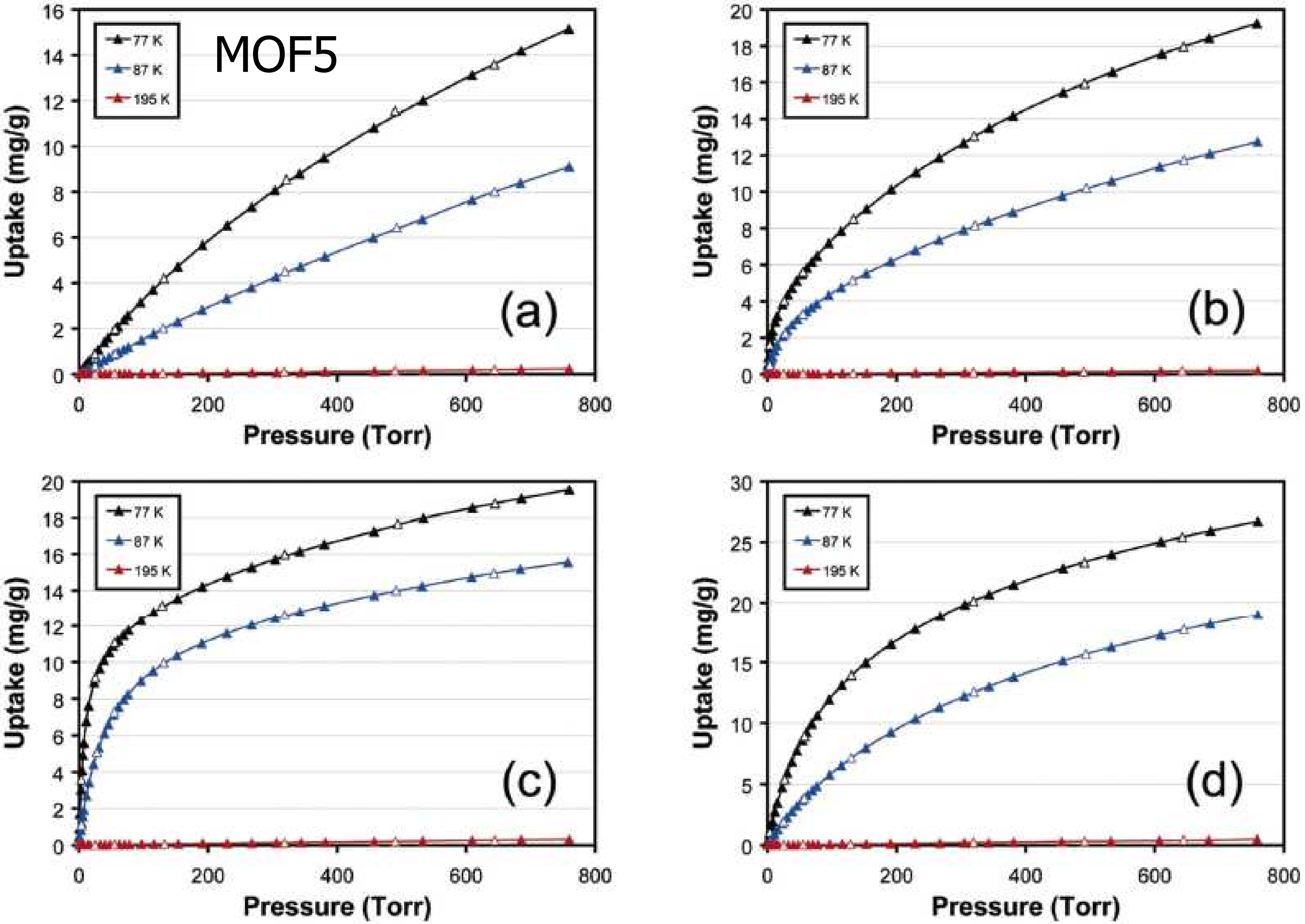
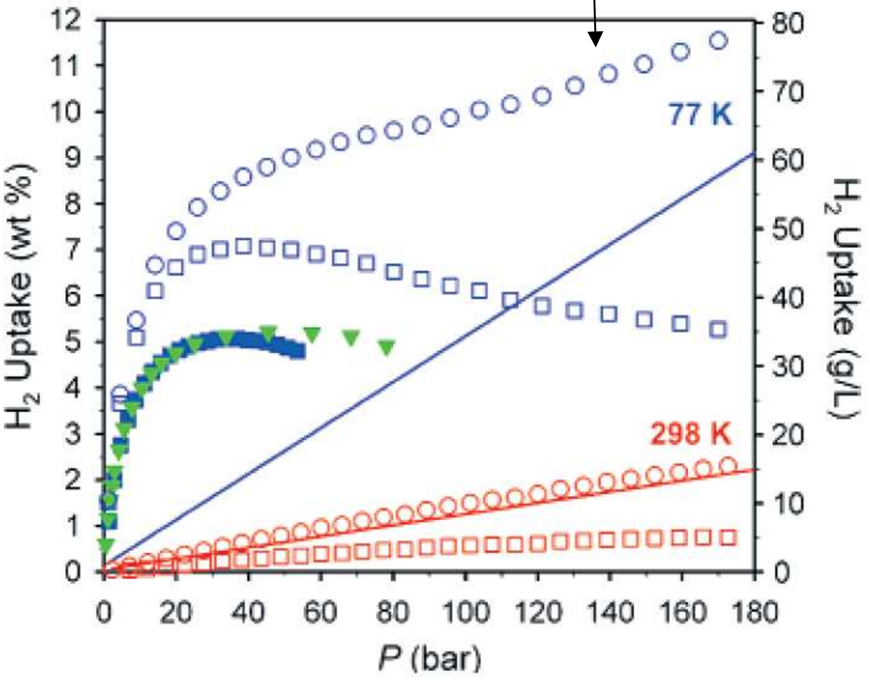


Figure 6. Dihydrogen adsorption isotherms measured at various temperatures for (a) IRMOF-1, (b) IRMOF-11, (c) MOF-74, and (d) HKUST-1. Note the different scales on ordinate axes. Adsorption data are shown as closed triangles, desorption as open triangles, and connecting traces are guides for the eye.

MOF5

In MOF5 about 1.5 wt% H_2 can be stored at 77K and 1 Bar.

At elevated pressures much larger storage is possible:
Up to 11.5 wt% at 120 Bar and 77K
(J. Am. Chem. Soc. 129 (2007) 14176)



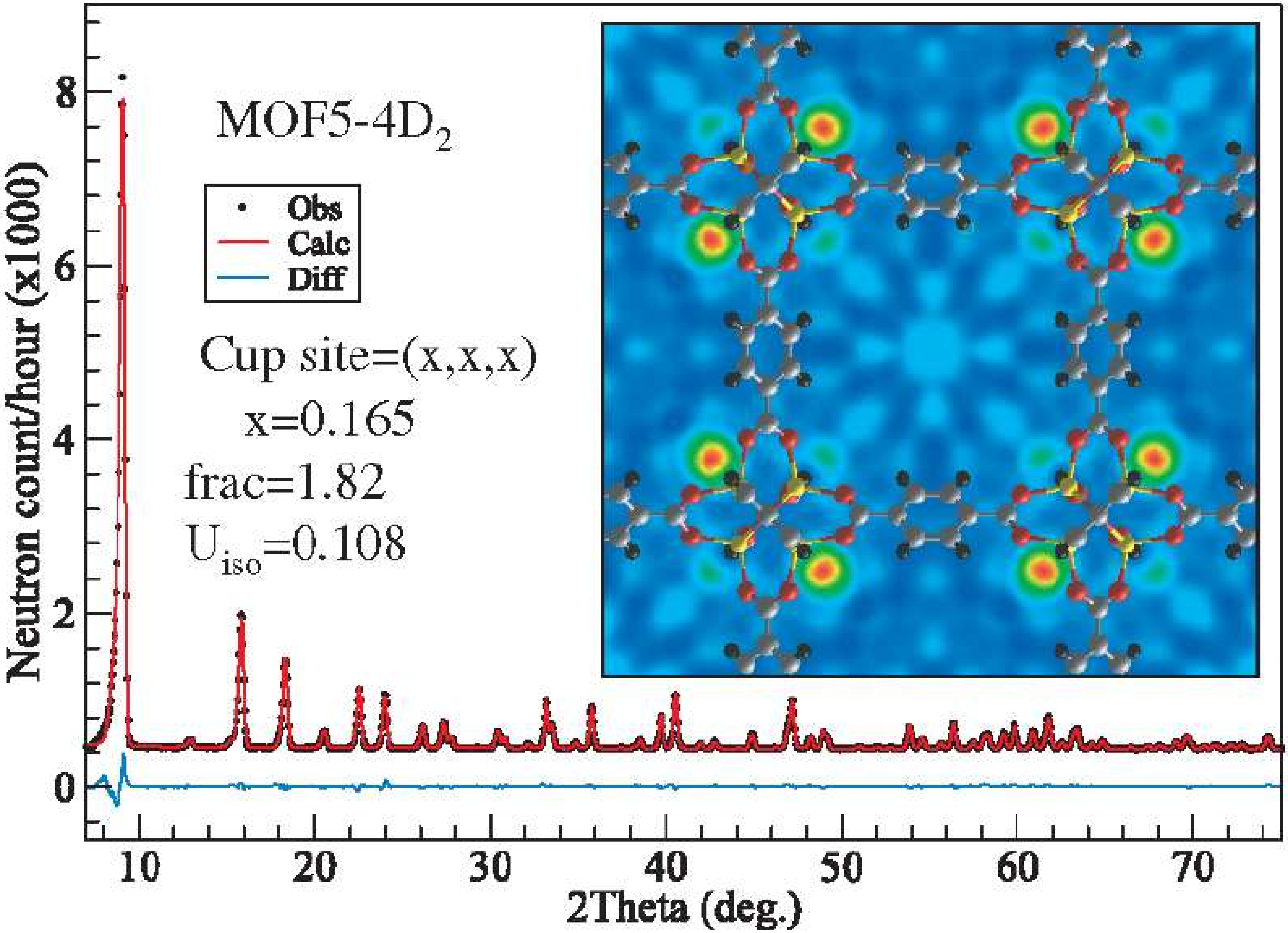
- ○ Total storage in sample material

- □ ‘Excess storage’ = total – $\rho_{bulk}V_{pores}$

  So this subtracts H_2 in the material that would have been stored even without the material being present.

Important questions:

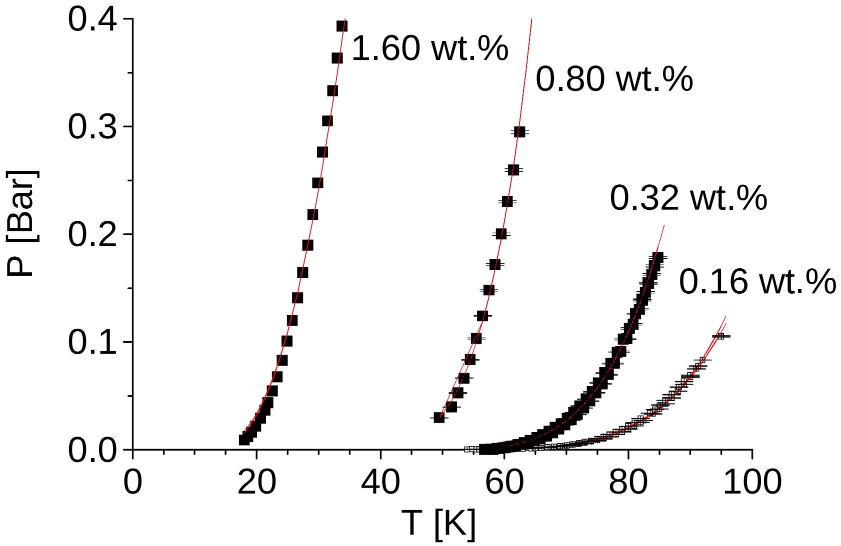
- what is adsorption interaction strength?
- where is hydrogen adsorbed in the material?
- stability of materials under hydrogen loading and unloading
- stability of materials under influence of impurities from e.g. air

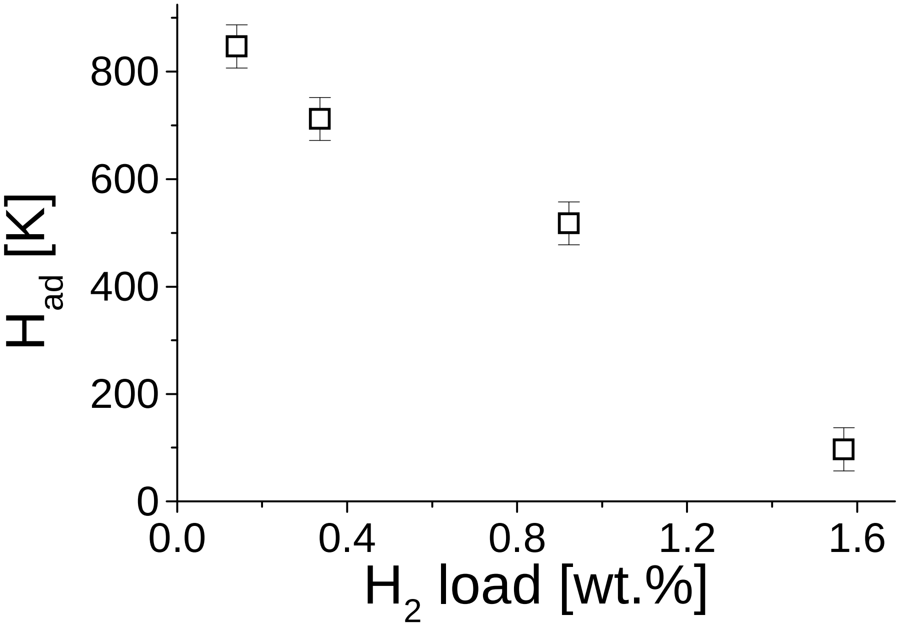


Neutron diffraction for locating D_2

Phys.Rev. Lett. 95 (2005) 215504

Macroscopic adsorption measurements





From the pressure as a function of temperature one can obtain an adsorption temperature using Langmuir theory.

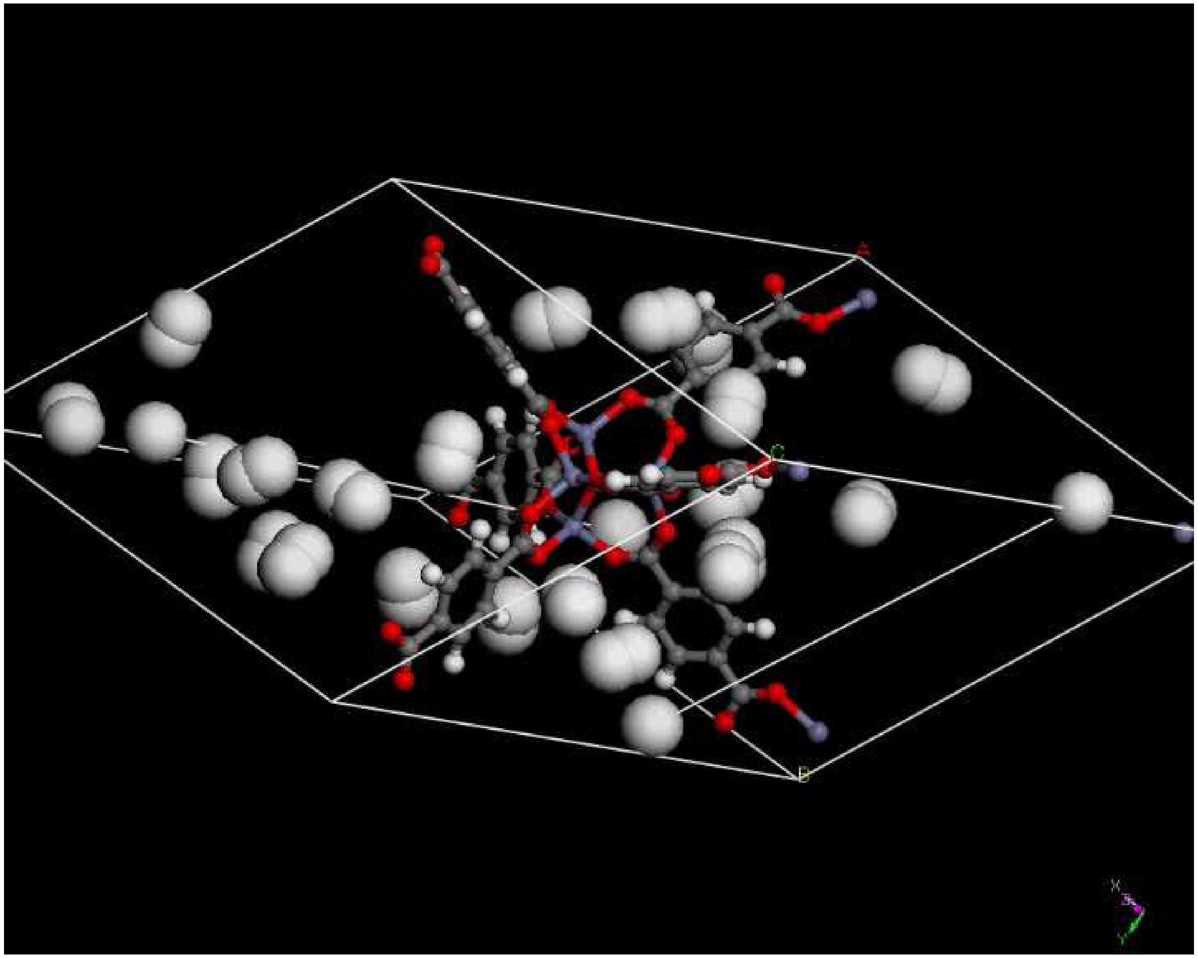
For MOF5: maximum ~ 850K

Compare nano carbons ~ 550 K

Chem.Phys. 317 (2005) 113.

Molecular dynamics

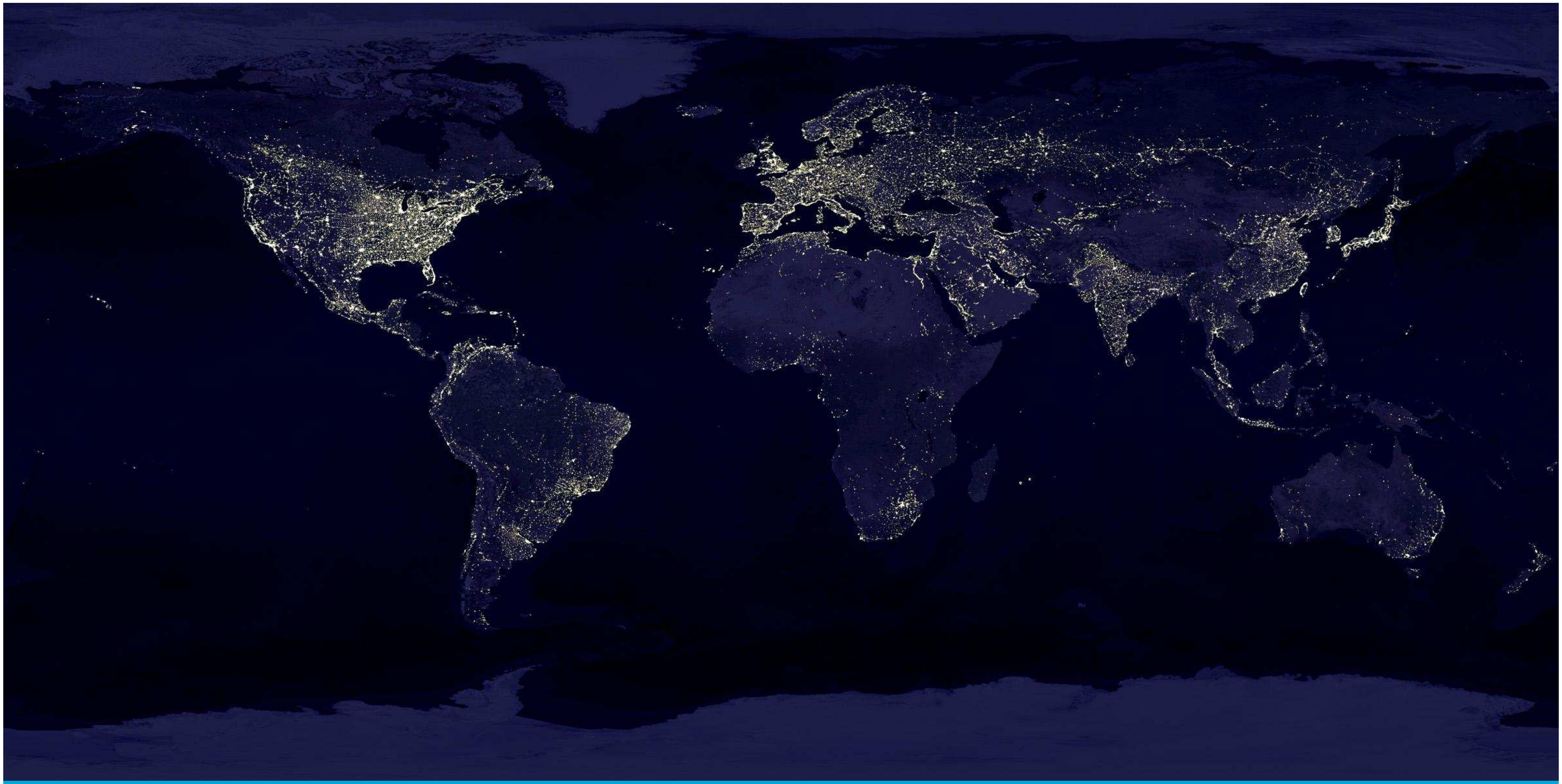
H_2 molecules in MOF5 at 150K



Basic results MOF’s

- adsorption capacities up to ~11.5 wt. % can be obtained at 77K and 120 Bar
- adsorption takes place at low T
- hydrogen can be loaded and unloaded in a fast way
- different adsorption sites are present:
  - -next to metal clusters
  - -next to organic spacer molecules
  - -on a second ‘layer’ in the pores
- adsorption energies are largest near the metal cluster:
  - ~ 800K maximum next to Zn of MOF5,
  - ~ 500K next to organic spacers
- surprising changes in the lattice can occur (next week).

Sustainable Hydrogen and Electrical Energy Storage



What is n on slide 18?

Elementary kinetic theory: relate n to quantities we know, P, V, T

Momentum transfer p of molecules / unit time gives a force:
Momentum transfer p_v of molecules with density n_v, mass m, certain velocity $v_{\perp A}$, during time interval t, and on surface A:

2 when molecule bounces back elastically

$$p_v = 2\; m\, v_{\perp A}\; (n_v\, v_{\perp A}\, t\, A) = 2m\, n_v\, v^2_{\perp A}\, t\, A$$

Sum over all v's: $p = \sum_v 2 n_v m v_{\perp A}^2 tA = Nm\overline{v_{\perp A}^2}tA$

N is now the total density

Only ½ the molecules fly towards surface A

In general: $v_{\perp A}^2 = \frac{1}{3}\overline{v^2}$ because $\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2}$ and $v_x^2 + v_y^2 + v_z^2 = v^2$

What is *n* ? continued

So $p = \frac{1}{3} N m \overline{v^2} t A$

The pressure *P* delivered by the momentum transfer equals the momentum transfer *p* divided by the time *t* and the surface area *A*:

$$P = \frac{1}{3} N m \overline{v^2}$$

From the Maxwell equations one can derive that $\frac{1}{3}\overline{v^2} = \frac{1}{8}\pi\left(\overline{v}\right)^2$

so $P = \frac{1}{8}\pi N m \left(\overline{v}\right)^2$

What is *n* ? continued

$$\longrightarrow \qquad \left(\bar{v}\right) = \sqrt{\frac{8P}{\pi N m}} = \sqrt{\frac{8PV_M}{\pi N_M m}} = \sqrt{\frac{8RT}{\pi m}}$$

using $PV_M = N_M RT$. (N_M number of molec in a mole, V_M mol. volume, N=density)
Now we finally come to *n*, the flux onto a certain surface area.

$$n = \frac{1}{4} N \left(\bar{v}\right) = \frac{1}{4}\frac{N_M}{V_M}\left(\bar{v}\right) = \frac{1}{4}\frac{N_M P}{RT}\sqrt{\frac{8RT}{\pi m}} = \frac{N_M P}{\sqrt{2\pi m R T}}$$

¼ results after integration over all possible angles