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Theoretical isosteric heat of adsorption calculation in the Henry's law region for carbon nanopores and nanocavities

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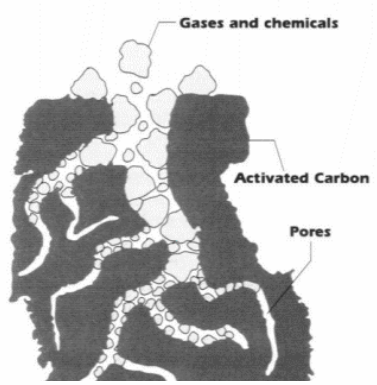
Outline

- Introduction
- Theory
- Results & Discussions
- Conclusions

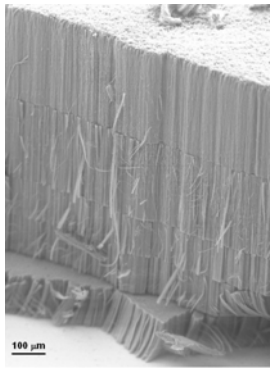
Gas adsorption ?

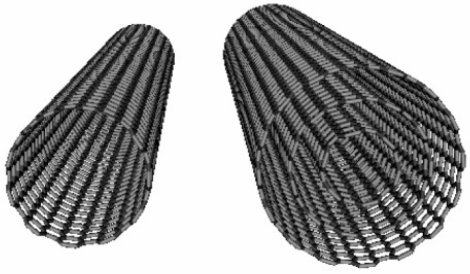
A process that occurs when a gas solute accumulates on the surface of a solid (**adsorbent**), forming a film of molecules or atoms (adsorbate).

Activated Carbon

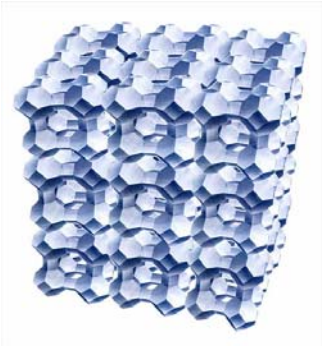


Carbon nanotubes

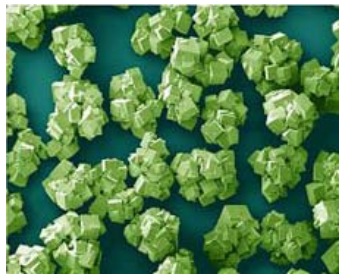


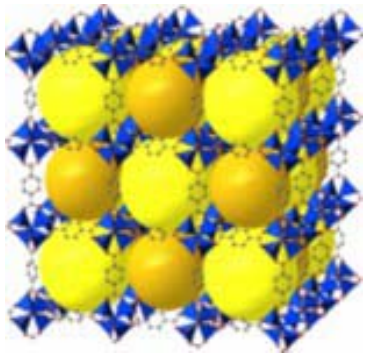


Zeolites



MOFs





Gas adsorption applications

Bulk separation or storage:
Oxygen supply
CO_2 capture, etc.

Purification:
Air quality
Packaging (silica gel)
Gas mask
Natural gas sweetening, etc.

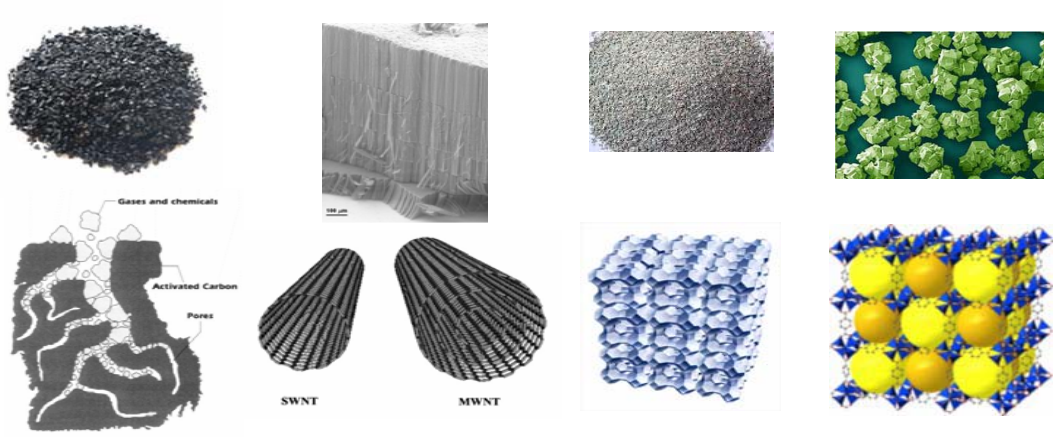
Space shuttle

Gas Mask

Pressure-swing application

Isotherm: adsorption equilibrium, adsorbent capacity
Heat of adsorption: heat effects, ease of regeneration

Motivation



Novel adsorbents

■ ■ ■

knowledge of the isosteric heat of adsorption for a molecule as a function of pore width is of great importance in the design and application of these novel materials.

Purification or storage application---high heat of adsorption is preferable because higher heats of adsorption mean stronger retention of gas molecules.

Pressure swing adsorption process---lower heat of adsorption is preferable because lower heats of adsorption reduce thermal swings and allow for easier regenerations.

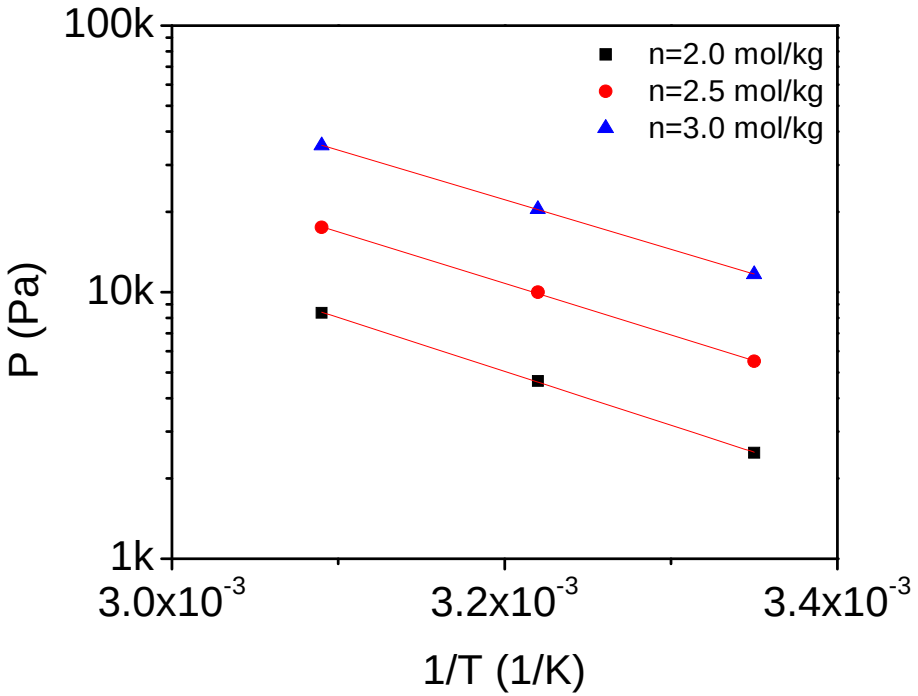
Isosteric heat of adsorption

1. Calorimetric measurement

2. Clausius-Clapeyron equation

$$q_{st}^{0} = -R\frac{\partial \ln P}{\partial 1/T}$$

3. Theoretical calculation



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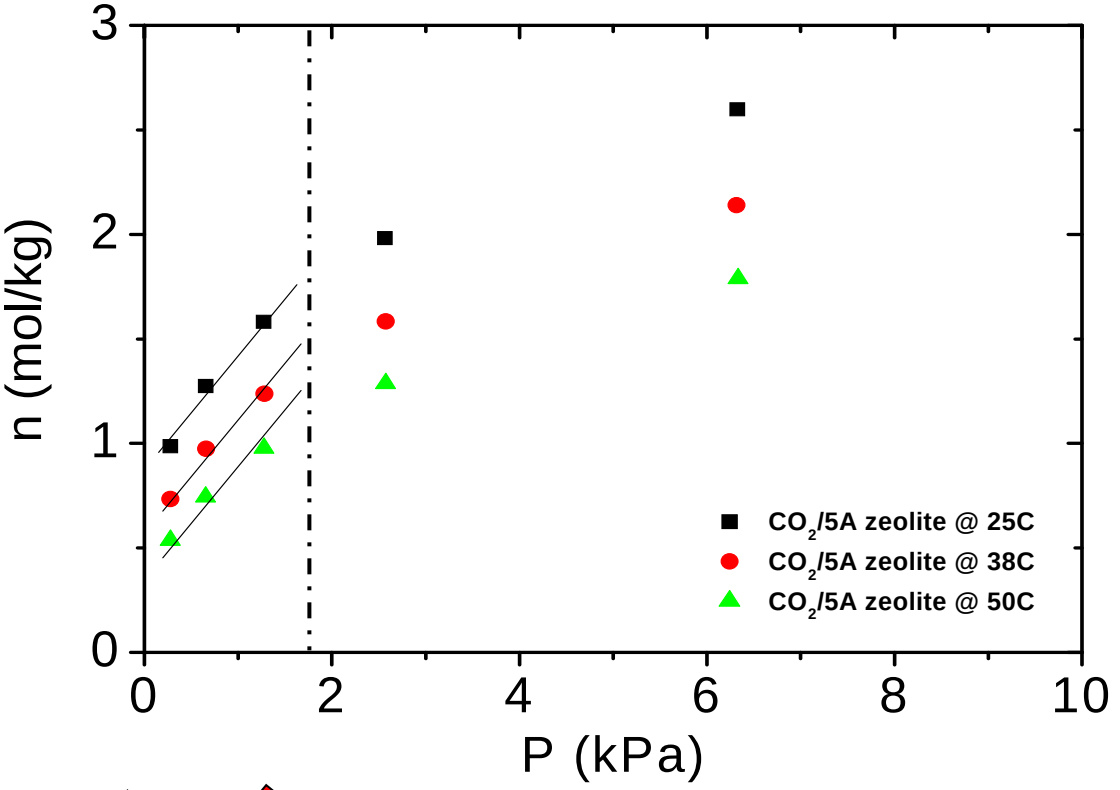
Henry's law region in adsorption

Henry' Law region

$n = k_H P$

k_H: Henry constant



$$\phi_{\text{total}} = \phi_{\text{adsorbate-adsorbent}} + \phi_{\text{adsorbate-adsorbate}}$$

Infinitesimal gas concentration

Theory and model

$$q_{\mathrm{st}}^{\mathrm{o}} = RT - N_{\mathrm{a}} \frac{\int_0^{Hc} V_{\mathrm{ext}}(r) \exp[-V_{\mathrm{ext}}(r)/kT]\, dr}{\int_0^{Hc} \exp[-V_{\mathrm{ext}}(r)/kT]\, dr}$$

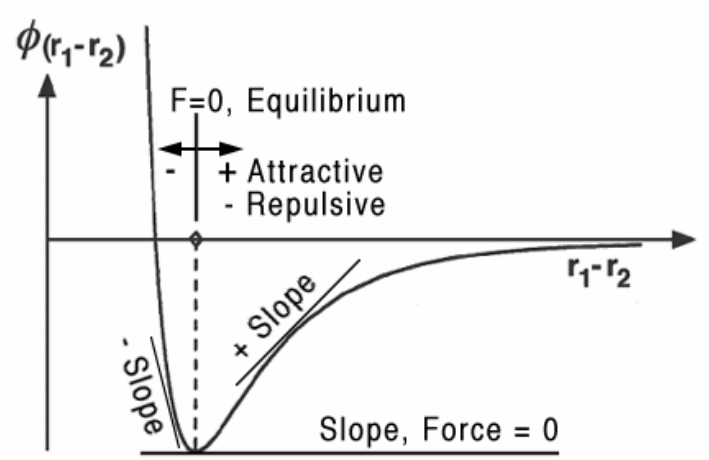
Steele WA. *The interaction of gases with solid surfaces*. 1974.

$V_{\mathrm{ext}}(r)$ is the external wall potential, which is different for different geometries.

Lennard - Jones potential

$$\Gamma_{\mathrm{sf}} = 4\epsilon_{\mathrm{sf}} \left[\left(\frac{\sigma_{\mathrm{sf}}}{r} \right)^{12} - \left(\frac{\sigma_{\mathrm{sf}}}{r} \right)^{6} \right]$$

where *r* is the interatomic distance



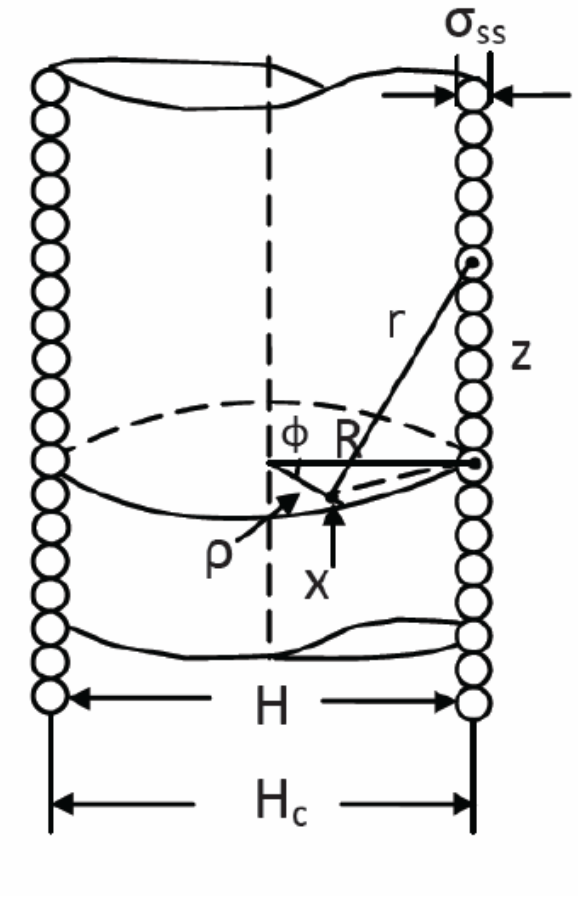
LJ parameters

Molecule	σ_{ff} (Å)	ϵ_{ff}/k (k)	σ_{sf} (Å)	ϵ_{sf}/k (k)
Ar	3.305	118.05	3.35	55.0
CH_4	3.82	148.2	3.60	64.4
CO_2	3.454	235.9	3.43	81.5
H_2	2.83	59.7	3.10	40.87
He	2.56	10.21	2.98	16.90
N_2	3.575	94.45	3.494	53.22

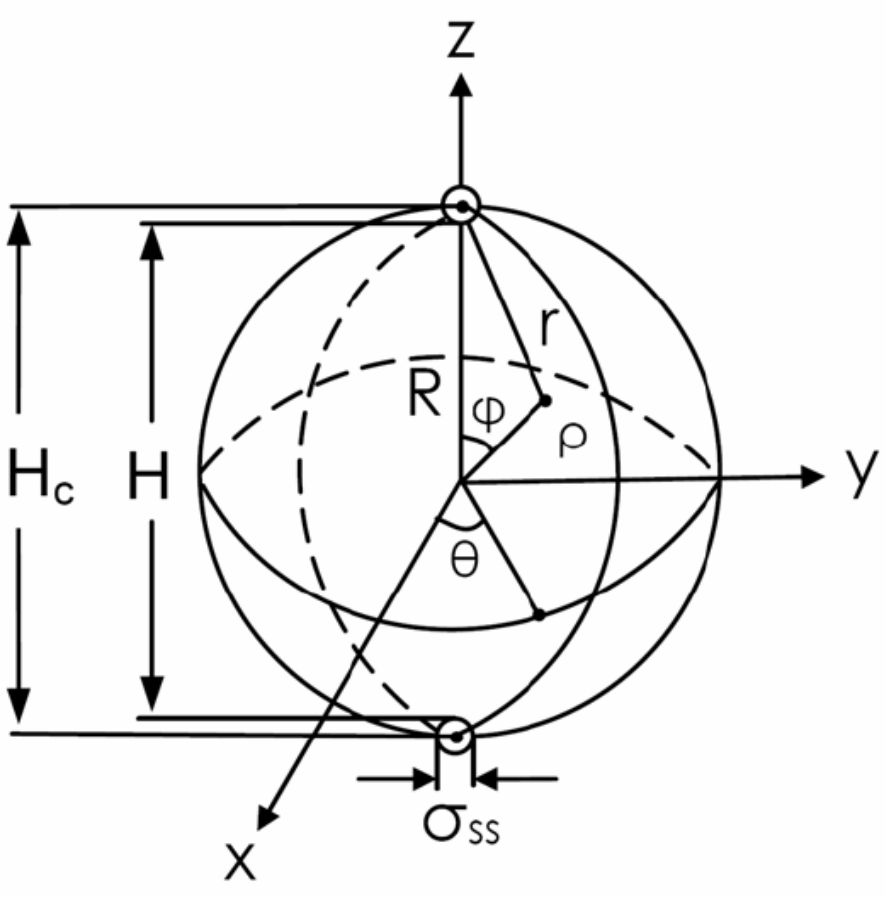
$$\sigma_{sf} = (\sigma_{ff} + \sigma_{ss})/2 \text{ and } \epsilon_{sf} = \sqrt{\epsilon_{ff}\epsilon_{ss}}$$ Lorentz-Berthelot combining rules

All parameters except for hydrogen and helium are acquired from the literature by using density functional theory (DFT) method to fit the experimental data.

Carbon nanopore and nanocavity

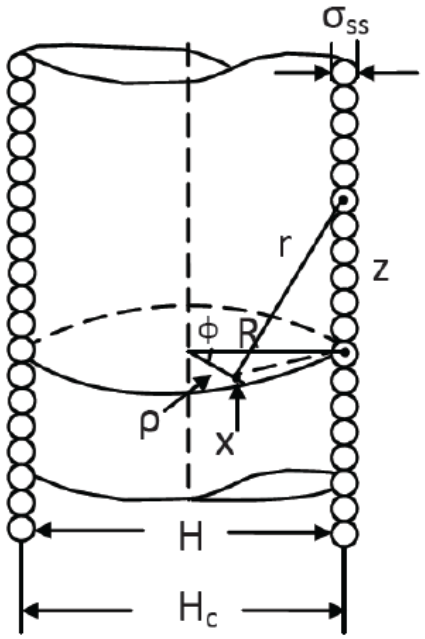


Cylindrical nanopore
SWNT



Spherical nanocavity
Fullerene (C60)

External wall potential - cylinder



$$V_{\text{ext}} = \int_A n_{\text{s}} \Gamma_{\text{sf}} \, d\alpha$$

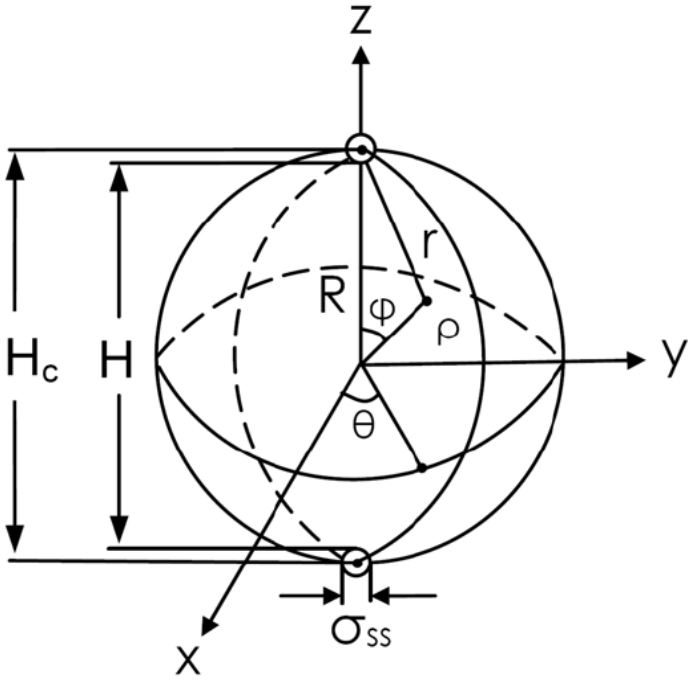
$$r^2 = z^2 + \rho^2 + R^2 - 2\rho R \cos\phi$$

Integrate over *z* and ϕ

$$V_{\text{ext, cyl}} = n_{\text{s}} \pi^2 \epsilon_{\text{sf}} \sigma_{\text{sf}}^2 \left\{ \frac{63}{32} \left[\frac{R-\rho}{\sigma_{\text{sf}}} \left(1 + \frac{\rho}{R}\right) \right]^{-10} \times F\left[-\frac{9}{2}, -\frac{9}{2}; 1; \left(\frac{\rho}{R}\right)^2 \right] \right.$$
$$\left. -3 \left[\frac{R-\rho}{\sigma_{\text{sf}}} \left(1 + \frac{\rho}{R}\right) \right]^{-4} \times F\left[-\frac{3}{2}, -\frac{3}{2}; 1; \left(\frac{\rho}{R}\right)^2 \right] \right\}$$

Tjatjopoulos et al. *J. Phys. Chem*. **1988**.

External wall potential - sphere



$$V_{\text{ext}} = \int_0^{2\pi} \int_0^{\pi} n_s \Gamma_{sf} R^2 \sin\phi \; d\phi d\theta$$

$$r^2 = R^2 + \rho^2 - 2\rho R \cos\phi$$

Integrate over θ and ϕ

$$V_{\text{ext, sphe.}} = 8\pi R^2 n_s \epsilon_{sf} \left[-\left(\frac{\sigma_{sf}}{R}\right)^6 \frac{1}{4(\rho/R)} \left(\frac{1}{(1-\rho/R)^4} - \frac{1}{(1+\rho/R)^4} \right) + \left(\frac{\sigma_{sf}}{R}\right)^{12} \frac{1}{10(\rho/R)} \left(\frac{1}{(1-\rho/R)^{10}} - \frac{1}{(1+\rho/R)^{10}} \right) \right]$$

Baksh et al. *AlChE J*. **1991**.

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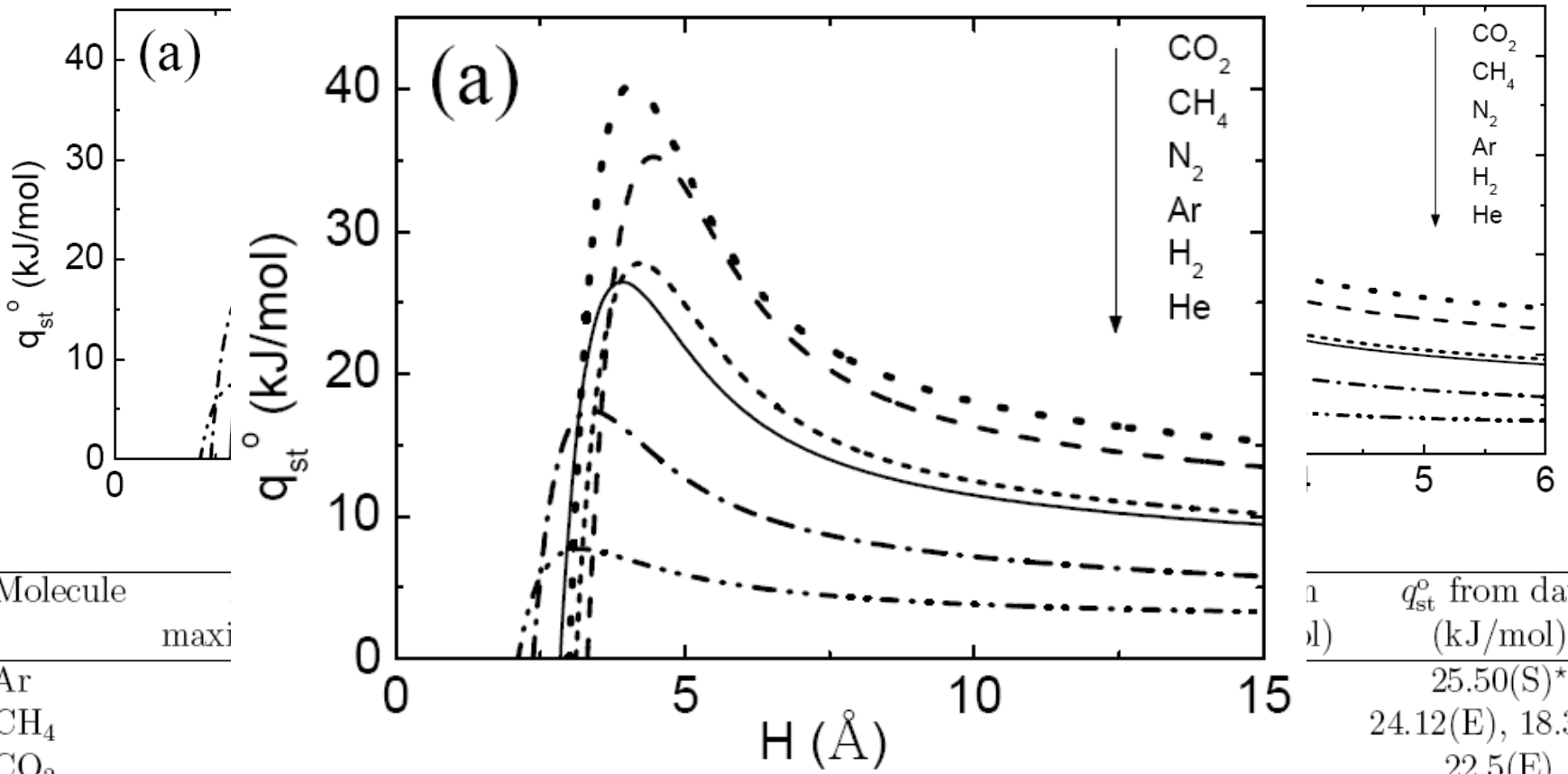
Cylindrical nanopore results



Molecule	maxi					q_{st}^{o} from data (kJ/mol)
Ar						25.50(S)*
CH_4						24.12(E), 18.3(E)
CO_2						22.5(E)
H_2	3.38	1.19	2.37	0.84	17.41	7.5(E)
He	3.18	1.19	2.12	0.83	7.72	3.58(E)
N_2	4.22	1.18	3.12	0.87	27.76	16.80(S), 9.17(E)

Empirical relationships

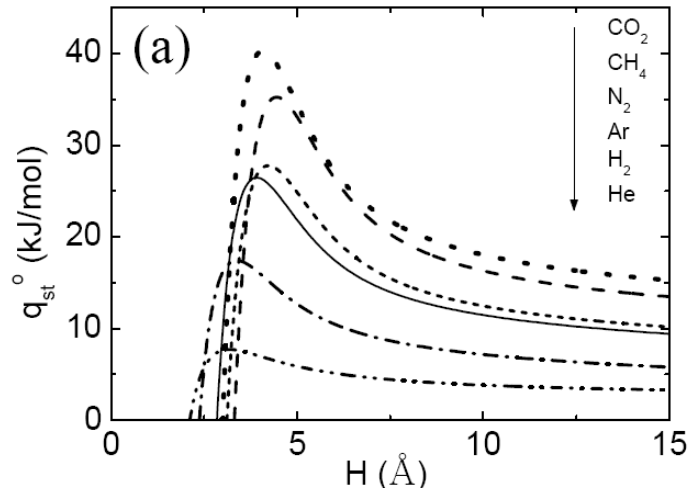
Geometry	Average dimensionless pore diameter for $q_{st}^{o} = \max$ $H_{c\ max}/\sigma_{sf}$	Average dimensionless pore diameter for $q_{st}^{o} = 0$ $H_{c\ zero}/\sigma_{sf}$
Slit-shaped	2.00	1.71
Cylindrical	2.18	1.86
Spherical	2.33	2.00

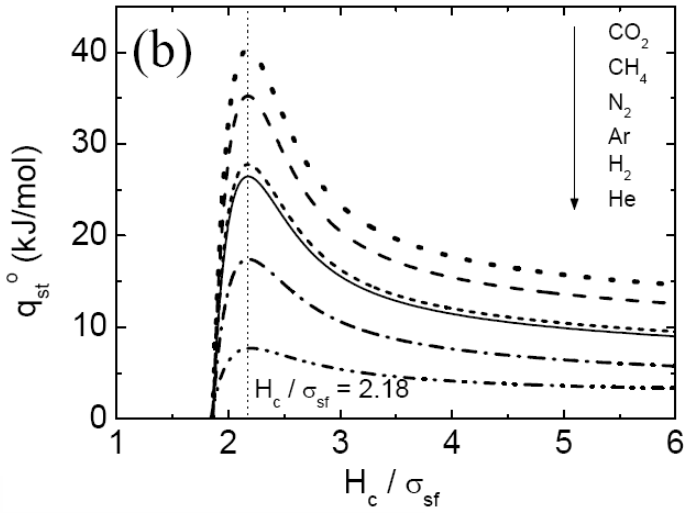
Slit-shaped results are from Schindler and LeVan. *Carbon* **2008**.

Predict the pore width where isosteric heat of adsorption is maximum or zero for non-polar or weakly polar gas molecules that have not been studied in this research

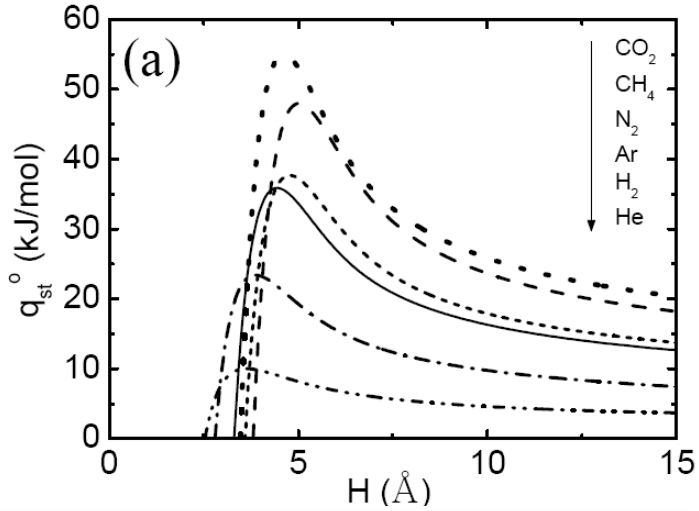
Comparison of results

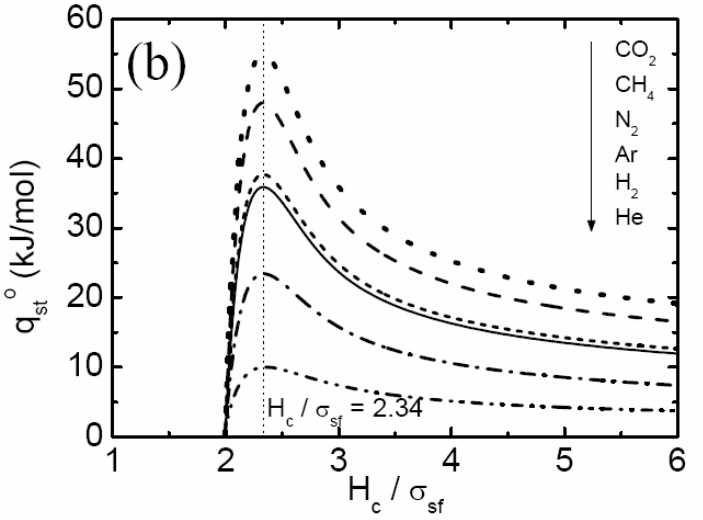
Cylindrical results



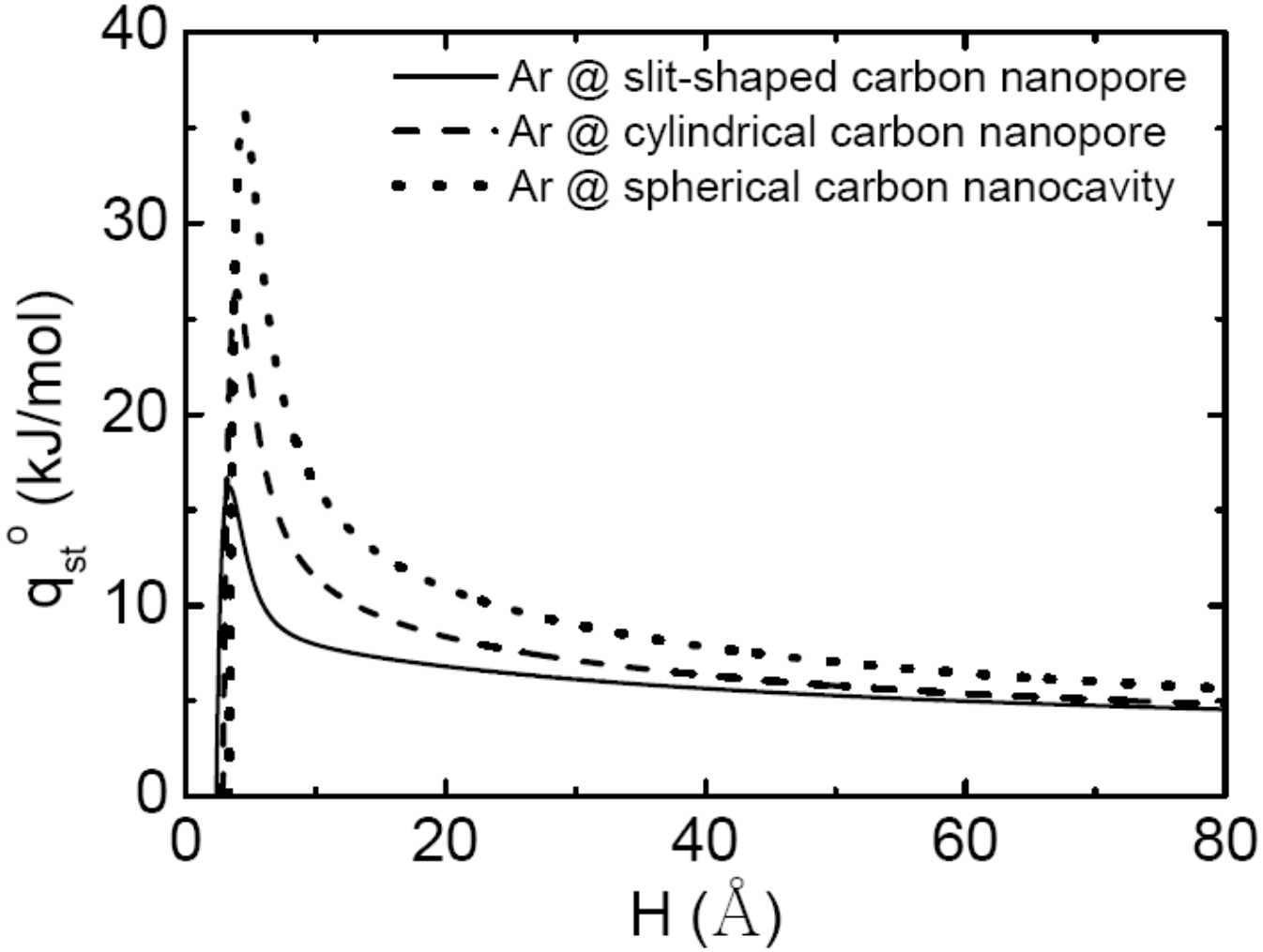


Spherical results

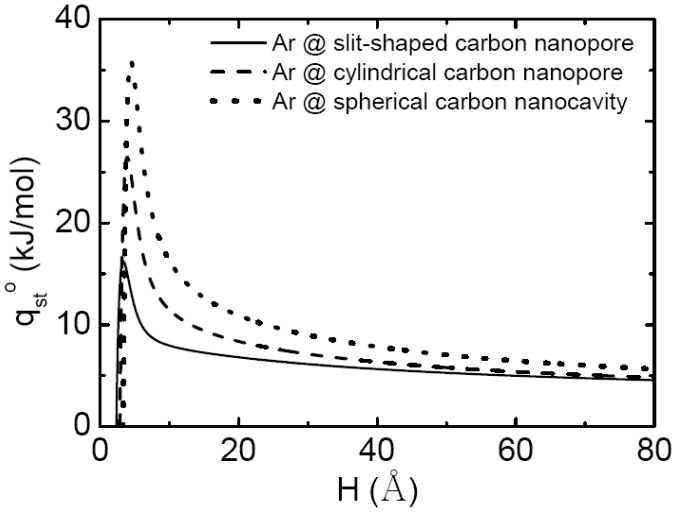




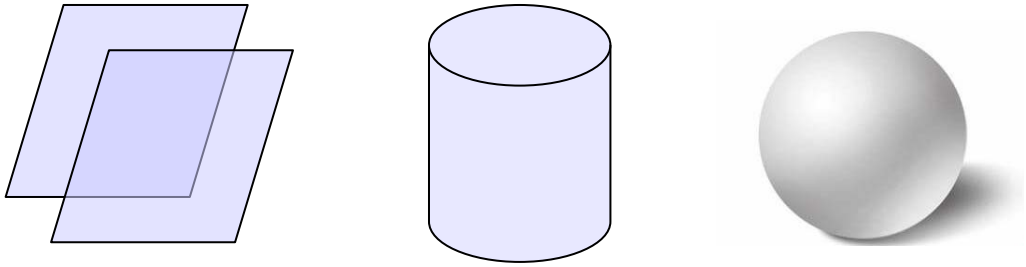
Argon example



Geometrical effect

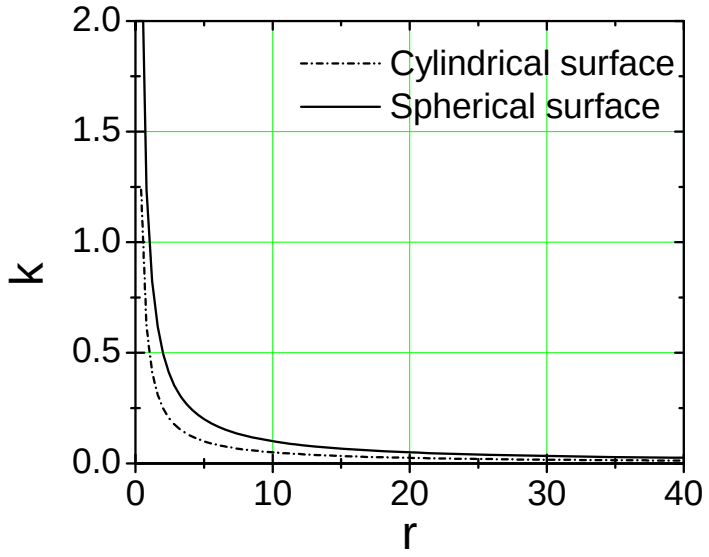


Slit Cylinder Sphere



k = surface mean curvature

k = 0 k = 1/(2r) k = 1/r



Conclusions

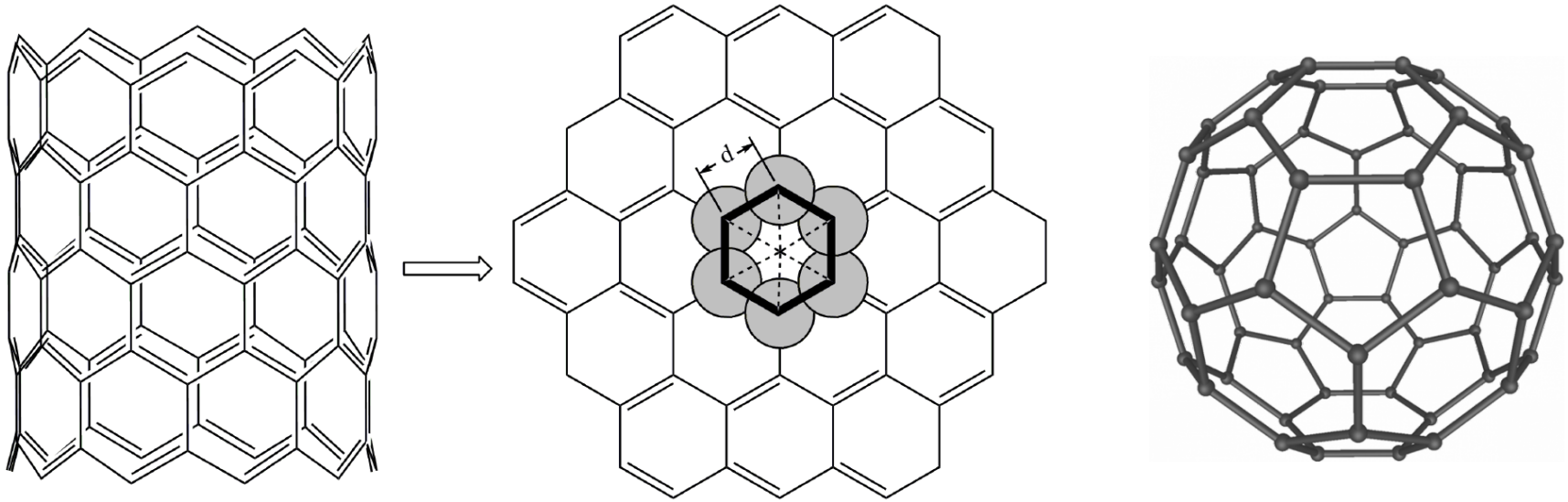
- Isosteric heat of adsorption in the Henry's law region has been calculated as a function of pore width for six gas molecules for cylindrical and spherical carbon surfaces.

- Constant linear relationships have been found between the pore diameter of maximum $q_{\mathrm{st}}^{\mathrm{o}}$ and the specific σ_{sf} for all of the gas molecules considered.

- Geometrical effects on the maximum $q_{\mathrm{st}}^{\mathrm{o}}$ have been ascribed to the difference of surface mean curvatures for different geometries.

Thank you!

Surface number density



C-C bond length: $d = 1.42 \text{Å}$ $\Longrightarrow$ $n_s = 3.82 \times 10^{19}\ \text{m}^{-2}$

Wilder et al. *Nature* **1998**.