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.

**Isotherm:** adsorption equilibrium, adsorbent capacity

**Heat of adsorption:** heat effects, ease of regeneration

Pressure-swing application

Space shuttle

Gas Mask
Motivation

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’s 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


\[ q_{st}^o = RT - N_a \frac{\int_0^{H_c} V_{ext}(r) \exp\left[-V_{ext}(r)/kT\right] dr}{\int_0^{H_c} \exp\left[-V_{ext}(r)/kT\right] dr} \]

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

**Lennard - Jones potential**

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

where \( r \) is the interatomic distance
LJ parameters

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\sigma_{ff}$ (Å)</th>
<th>$\epsilon_{ff}/k$ (k)</th>
<th>$\sigma_{sf}$ (Å)</th>
<th>$\epsilon_{sf}/k$ (k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>3.305</td>
<td>118.05</td>
<td>3.35</td>
<td>55.0</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.82</td>
<td>148.2</td>
<td>3.60</td>
<td>64.4</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>3.454</td>
<td>235.9</td>
<td>3.43</td>
<td>81.5</td>
</tr>
<tr>
<td>H$_2$</td>
<td>2.83</td>
<td>59.7</td>
<td>3.10</td>
<td>40.87</td>
</tr>
<tr>
<td>He</td>
<td>2.56</td>
<td>10.21</td>
<td>2.98</td>
<td>16.90</td>
</tr>
<tr>
<td>N$_2$</td>
<td>3.575</td>
<td>94.45</td>
<td>3.494</td>
<td>53.22</td>
</tr>
</tbody>
</table>

Lorentz-Berthelot combining rules

$$\sigma_{sf} = (\sigma_{ff} + \sigma_{ss})/2$$ and $$\epsilon_{sf} = \sqrt{\epsilon_{ff}\epsilon_{ss}}$$

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**

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

\[
-3 \left[ \frac{R - \rho}{\sigma_{sf}} (1 + \frac{\rho}{R}) \right]^{-4} \times F \left[ -\frac{3}{2}, -\frac{3}{2}; 1; \left( \frac{\rho}{R} \right)^2 \right] \}
\]

Integrate over \( z \) and \( \phi \)

\[
V_{\text{ext}} = \int_A n_s \Gamma_{sf} \, d\alpha
\]

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

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 \( \theta \) and \( \phi \)

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

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Cylindrical nanopore results

### Table of Results

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$q_{st}^{o}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>3.38</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>3.18</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>4.22</td>
</tr>
<tr>
<td>H$_2$</td>
<td>1.19</td>
</tr>
<tr>
<td>He</td>
<td>1.18</td>
</tr>
<tr>
<td>N$_2$</td>
<td>1.18</td>
</tr>
</tbody>
</table>

### Graphical Representation

- **Graph (a)**
  - $q_{st}^{o}$ (kJ/mol) vs. $H$ (Å)
  - Data points for various molecules:
    - CO$_2$, CH$_4$, N$_2$, Ar, H$_2$, He

### Additional Information
- $q_{st}^{o}$ from data
- Units: (kJ/mol)

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$q_{st}^{o}$ from data</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO$_2$</td>
<td>25.50 (S)*</td>
</tr>
<tr>
<td>CH$_4$</td>
<td>24.12 (E), 18.3 (E)</td>
</tr>
<tr>
<td>N$_2$</td>
<td>22.5 (E)</td>
</tr>
<tr>
<td>Ar</td>
<td>7.5 (E)</td>
</tr>
<tr>
<td>H$_2$</td>
<td>3.58 (E)</td>
</tr>
<tr>
<td>He</td>
<td>16.80 (S), 9.17 (E)</td>
</tr>
</tbody>
</table>
### Empirical relationships

<table>
<thead>
<tr>
<th>Geometry</th>
<th>Average dimensionless pore diameter for $q^o_{st} = \text{max}$</th>
<th>Average dimensionless pore diameter for $q^o_{st} = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slit-shaped</td>
<td>$H_{c\text{ max}}/\sigma_{sf}$ 2.00</td>
<td>$H_{c\text{ zero}}/\sigma_{sf}$ 1.71</td>
</tr>
<tr>
<td>Cylindrical</td>
<td>$H_{c\text{ max}}/\sigma_{sf}$ 2.18</td>
<td>$H_{c\text{ zero}}/\sigma_{sf}$ 1.86</td>
</tr>
<tr>
<td>Spherical</td>
<td>$H_{c\text{ max}}/\sigma_{sf}$ 2.33</td>
<td>$H_{c\text{ zero}}/\sigma_{sf}$ 2.00</td>
</tr>
</tbody>
</table>


*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

\[ q^0_{st} \text{ (kJ/mol)} \]

\[ H (\text{Å}) \]

\[ H_c / \sigma_{st} \]

\[ H_c / \sigma_{st} = 2.18 \]

\[ H_c / \sigma_{st} = 2.34 \]
Argon example

\[ q_{st}^0 \text{ (kJ/mol)} \]

- \( \text{Ar @ slit-shaped carbon nanopore} \)
- \( \text{Ar @ cylindrical carbon nanopore} \)
- \( \text{Ar @ spherical carbon nanocavity} \)

\[ H \text{ (Å)} \]

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Geometrical effect

$k = 0 \quad k = 1/(2r) \quad k = 1/r$

$k = \text{surface mean curvature}$

1. Ar @ slit-shaped carbon nanopore
2. Ar @ cylindrical carbon nanopore
3. Ar @ spherical carbon nanocavity

Spherical surface

Cylindrical surface

Slit

Cylinder

Sphere

$q_{st} (\text{kJ/mol})$ vs $H (\text{Å})$
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 $q_{st}^o$ and the specific $\sigma_{sf}$ for all of the gas molecules considered.

- Geometrical effects on the maximum $q_{st}^o$ have been ascribed to the difference of surface mean curvatures for different geometries.
Thank you!
Surface number density

C-C bond length: \( d = 1.42\,\text{Å} \)

\[ n_s = 3.82 \times 10^{19} \, \text{m}^{-2} \]