Determination of the enthalpy of adsorption of hydrogen in activated carbon at room temperature


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ABSTRACT

The development of high-performance materials for hydrogen storage by adsorption requires detailed understanding of the adsorbate-adsorbent interactions, e.g., the enthalpy of adsorption \( \Delta H \), which measures the interaction strength. The determination of \( \Delta H \) for a weakly adsorbing gas such as hydrogen in a carbonaceous porous material is difficult experimentally, normally requiring measuring two cryogenic adsorption isotherms. Here we demonstrate a calculation of \( \Delta H \) based on ca. room temperature adsorption isotherms at 273 K and 296 K using the Clausius-Clapeyron equation. This requires an estimation of the volume of the adsorbed film (~40%, ~12% of the total pore volume at 77 K, 296 K, respectively) obtained from fits of the excess adsorption isotherms to an Ono-Kondo model with the auxiliary use of a fixed point corresponding to the saturation film density (estimated as 100 ± 20 g/L) which appears to be remarkably sample and temperature independent, i.e., a property of the adsorbate. The calculated room temperature enthalpy of adsorption \( \Delta H = 8.3 \pm 0.4 \text{ kJ/mol} \) is in excellent agreement with the low-coverage cryogenic

HIGHLIGHTS

- New method to determine the adsorption enthalpy \( \Delta H \) of hydrogen at room temperature.
- Smaller uncertainty for \( \Delta H \) than results calculated using common assumptions.
- Estimation of saturation film density, sample and temperature independent.
- Estimation of adsorbed film volume (significantly smaller than pore volume).
- Measurements performed on a large-volume (5.3 L) high-pressure vessel.

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GRAPHICAL ABSTRACT
Introduction

Due to the environmental impact and finite supply of conventional fossil fuels, substantial steps are needed to seek a cleaner, more sustainable fuel source. Hydrogen-based systems only produce water as a byproduct, making it one of the most desirable alternative fuel sources, especially when produced through sustainable and non-polluting methods such as solar electrolysis or biogas [1]. Hydrogen fuel cell systems can be smaller, weigh less, and can be charged in minutes instead of hours compared to batteries [2]. The largest hurdle remains the storage of the gas itself: for hydrogen to be a viable fuel source its low volumetric energy density at ambient conditions (0.0107 MJ/L) must be increased by orders of magnitude to approach the energy density of liquids such as gasoline (31.1 MJ/L) [3]. Current hydrogen-based systems rely solely on liquefying or compressing the gas. Liquefaction requires expensive refrigeration systems to achieve sufficiently low temperatures (~20 K) [4]. Prototype fuel cell vehicles using compression operate at pressures up to 700 bar [4,5]; this level of compression requires large, heavy metallic or expensive carbon fiber gas cylinders that occupy a significant amount of cargo space for storage limiting the passenger/cargo capacity of the vehicle [6,7]. In addition to the practical difficulties of storing hydrogen at such extreme conditions, a significant amount of energy is lost during liquefaction or compression (~1/3 and ~1/5 of the heating value of hydrogen) [8]. Alternatively, systems utilizing adsorption can greatly increase the stored energy density. Adsorbent materials with nanoporous structures utilize the van der Waals attraction between the adsorbent and the adsorbate molecules to create a high density film [9]. Various factors, however, make this procedure difficult for hydrogen: its weak binding energy makes the measurements difficult at room temperature, and uncertainties in the determination of cold vs. warm volumes. Additionally, a more fundamental aspect is the fact that the CC equation requires the determination of absolute adsorption whereas experimentally only the excess adsorption is measured; the conversion between these requires knowledge of the adsorbed film volume which has been not measurable. This has led to assumptions/approximations that result in large uncertainties in the determination of ΔH.

In this study we have constructed a very large volume sample vessel (5.3-L) which is substantially larger than most previously existing hydrogen storage characterization systems. The large sample volume resulting relatively large amounts of adsorbed hydrogen result in very reliable ca. room temperature excess adsorption isotherms. We then propose a method to determine the adsorbed film volume from Ono-Kondo model fits of the excess adsorption isotherms with the auxiliary use of a fixed point corresponding to the saturation film density which appears to be remarkably sample and temperature independent (a property of the adsorbate). This allows the calculation of absolute adsorption isotherms which then are used to obtain the room temperature enthalpy of adsorption ΔH. The method presented here results in significantly lower uncertainties compared to the broad range permitted by the most common assumptions and lacks the unphysical rise with coverage sometimes reported. The results should be applicable to a wide range of samples and temperatures.

Experimental

Adsorbent preparation and characterization

The samples utilized in this work are comprised of monoliths created from a commercially available precursor powdered...
activated carbon (PAC): MWV-0260 (MeadWestVaco). The
c hemical activation was by means of KOH at high temperature
[25,31,32]. Carbonaceous adsorbent materials were chosen for
this work because they are able to maintain their high storage
capacities while withstanding extreme mechanical stress [33].
The precursor PAC was mixed using a rock tumbler with the
binder (polyvinylidene chloride-co-vinyl chloride) (PVDC) in
a 0.5:1 binder to PAC ratio. Then 0.5 kg of the mixture was
placed inside a cylindrical steel die at 27 °C in 0.1 kg in-
crements where a 760-bar compressive stress was applied
after each addition. The monoliths were then heated to 305 °C
under stress before being allowed to cool for 16 h while
maintaining the mechanical stress. These carbon monoliths
were pyrolized at 700 °C for 1.5 h under nitrogen prior to
measurements. The procedure results in remarkably consis-
tent samples; further detail about the production and char-
acterization of the monoliths can be found in the work by
Rash et al. [34] and in U.S patent numbers 8,691,177 [35] and
8,926,932 [36]. For our work, a 2.86 kg batch of monoliths,
filling the 5 L sample vessel, was studied (henceforth dubbed
BR-0311).
Subcritical nitrogen isotherms on PAC MWV-0260 and
small samples of BR-0311 were measured using a Quantach-
rome Autosorb-1. Results are summarized in Table 1. The
Brunauer-Emmett-Teller (BET) [37] surface areas \( S_{\text{BET}} \) were
measured using a pressure range of 0.03–0.1 \( P/P_0 \). The cu-
mulative pore volumes \( V_{\text{pore}} \) were measured at 0.995 \( P/P_0 \) by
assuming liquid densities within the pores. The pore volume
only includes void volume within individual grains and does
not include intergranular void space. The skeletal densities
\( \rho_{\text{ske}} \) were measured with helium pycnometry. These \( \rho_{\text{ske}} \) fall
within the typical range of values for amorphous carbon
(1.8–2.1 g/cm³) [25]. The void fraction or porosity is deter-
mined by
\[
\phi = \frac{V_{\text{pore}}}{V_{\text{pore}} + V_{\text{ske}}} = \left(1 + \left(\frac{\rho_{\text{ske}}}{\rho_{\text{gas}}} V_{\text{pore}}\right)^{-1}\right)^{-1}
\] (1)
Pore size distributions (PSD) were calculated using
quenched solid-state density functional theory (QSDFT)
[38–42] assuming slit shaped pores (see Fig. 1). The PSDs for
both materials exhibit consistent features. There is an overall
reduction from the monolith production process. Some pores
were likely clogged with the binder or crushed from the
intense mechanical stress. Surface areas and pore volumes
can also be reduced from doping the material with other ele-
ments such as Boron [43]. The varying pore widths correspond
to varying deepness of the potential wells [8,25,44], see Fig. 2:
narrower pores where the van der Waals potential of each side
of the pore overlap are deep while wider pores have shallower
potentials. Numerical simulations involving ensemble aver-
ages of different pore sizes weighted by the experimental
PSD’s [45] are consistent with the idea that narrower pores

predominantly adsorb the gases at lower coverage while wider
pores become more important once the deeper, narrow pores
are saturated.

**Hydrogen adsorption**

Gravimetric excess adsorption measurements were taken on
two instruments. A large sample (2.86 kg) was measured with
our “10-L Storage System” (10LSS). The 10LSS consists of two
5.3-L modular tanks, filling/discharging mass flow meters, and
thermal bath vessels, see Fig. 3. One of the 5.3-L tanks was
packed with the 2.86 kg of monoliths. A small sample
(~300 mg, 1 cm³) was measured on a Hiden Isochema HTP1-V.
The gravimetric excess adsorption is the only directly
measurable quantity that requires no assumptions about the
pore volumes [46], it is calculated from experimental data:
\[
G_{\text{ex}}(P) = \frac{m_{\text{H}_2,\text{tank}}}{m_s} - \frac{\rho_{\text{gas}}}{m_s} (V_{\text{tank}} - V_{\text{ske}}).
\] (2)
where \( m_s \) is the sample mass, \( m_{\text{gas}} \) is the gas density at the given pressure \( P \), \( V_{\text{tank}} \) is the volume of the tank or cell, and \( V_{\text{skeL}} \) is the volume of the carbon, (determined with helium pycnometry). In our analysis, in order to mitigate uncertainties \[47\], we ensured all instruments were well calibrated and leak proof, that samples were outgassed, thermally controlled, and that ultra-purified hydrogen gas (99.999%) was used. The extremely large sample size aided in reducing the relative error of our excess adsorption measurements. 

Gravimetric excess adsorption measurements are in excellent agreement (overall ~2%) between both aforementioned instruments at two different temperatures, see Fig. 4.

Additional metrics of interest, especially in engineering or applications are the gravimetric and volumetric storage capacities; these are presented for monolithic activated carbon BR-0311 in Appendix A.

Results and discussion

The enthalpy of adsorption \( \Delta H \) of a gas onto a surface is one of the most important adsorption characteristics; its value along with the specific surface area determine the overall performance of the material for storage or gas separation \[31,48,49\]. Normally, the determination of \( \Delta H \) for hydrogen is challenging; a direct determination requiring the use of very sensitive microcalorimeters \[50\]. Instead, a common approach is to apply the Clausius-Clapeyron equation to two isotherms at two (usually close) temperatures \[9,32\]:

\[
\Delta H = \frac{RT_1}{T_2 - T_1} \ln \frac{P_2}{P_1},
\]

where \( T_1 \) and \( T_2 \) are the temperatures at which the two adsorption measurements were taken and \( P_1 \) and \( P_2 \) are the pressures at which a constant number of particles exist in the adsorbed phase.

As discussed in Refs. \[51\], the isosteric condition is equal absolute adsorption \( G_{\text{abs}} \). Experimentally, only the excess adsorption \( G_{\text{ex}} \) is measured directly. In addition, cryogenic adsorption isotherms have obvious technical complications (e.g., well-controlled refrigeration/cryostats) and careful calibration (e.g., cold vs. hot volumes) \[52\]. However, if the volume of the adsorbed film \( V_{\text{film}} \) were known, it would be possible to calculate the former:

\[
G_{\text{abs}} = G_{\text{ex}} + \rho_{\text{gas}} V_{\text{film}}.
\]

Unfortunately, \( V_{\text{film}} \) is not directly observable. Common assumptions utilized in the literature are \( V_{\text{film}} = 0 \) (i.e., \( G_{\text{ex}} \), a significant underestimation) and \( V_{\text{film}} = V_{\text{pore}} \) (which generally overestimates \( G_{\text{abs}} \) since obviously \( V_{\text{film}} \leq V_{\text{pore}} \) \[53–56\]. These assumptions result either overestimation or underestimation of \( \Delta H \), respectively \[53–56\]. Here, we will show how to combine high quality high temperature \( G_{\text{ex}}(P,T) \) measurements at ca. room temperature with cryogenic determinations of the adsorbed film density at saturation \( \rho_{\text{film,sat}} \) to obtain reasonable estimations of the film volume \( V_{\text{film}} \), which enable the determination of the absolute adsorption isotherms \( G_{\text{abs}}(P,T) \), and thus the enthalpy of adsorption from the Clausius-Clapeyron equation. The procedure is depicted in Fig. 5 and described in detail in what follows.

Cryogenic determination of adsorbed film densities and volumes

The procedure is to calculate the volume of the adsorbed film from additional experiments. For sufficiently high gas pressures (or \( \rho_{\text{gas}} \), when the film density “saturates”, i.e., \( \rho_{\text{film,sat}} \approx \rho_{\text{film,sat}} \), \( G_{\text{abs}} \approx \text{constant} \), thus using Eq. (6) the volume of the film can be determined:

\[
V_{\text{film}} = \frac{G_{\text{ex}} - \rho_{\text{gas}} V_{\text{film}}}{\rho_{\text{film,sat}}}
\]
temperature determination of the adsorbed film density at saturation densities and volume, use the Ono-Kondo relation (Eq. (5)).

The excess adsorption isotherms exhibit a linear decay with the gas density (Eqs. (5) and (6)). Fig. 7 (a) shows adsorption isotherms for a variety of activated carbons including powders, monoliths and polymer-based materials at 77 K. Donhke et al. [68] have shown that, in this regime, the saturated adsorbed film volume is given by the slope $V_{film} = dG_{ex}/d\rho_{gas}$, and the extrapolation to where the line crosses the abscissa ($G_{ex} = 0$) provides a good estimate for the saturated film density, $\rho_{film,sat}$. It is remarkable that in all samples, the estimation of $\rho_{film,sat}$ (97–107 g/L) is higher than that of liquid H2 (71 g/L) and is quite independent of the sample specific surface area, see Fig. 7 (b) [66,68,69]. Additionally, the almost linear relation between $V_{film}$ and specific surface area, in Fig. 7 (c), indicate a common film thickness $t_{film} = V_{film}/S_{BET} \approx 3$ Å which is significantly lower than the typical pore sizes $> 7$ Å. Across a wide range of temperatures (77–173 K), the estimation of $\rho_{film,sat}$ (100–112 g/L) on BR-0311 is also higher than that of liquid H2 (71 g/L) and is quite independent of temperature, see Fig. 8 (b) [68,69]. Additionally, $V_{film}$ tends to decrease with increasing temperature, see Fig. 8 (c) which, as an aside, is similar to what was observed with methane as temperatures increase [70].

The fact that $\rho_{film,sat}$ is sample and temperature independent, at least empirically, makes it a property of the adsorbate, i.e., for a given material, a cryogenic temperature determination of $\rho_{film,sat}$ would be valid at almost any other temperature (and likely may even be valid to other materials). The reason for this robustness is that at saturation the film is densely packed so that the dominant effect is the hydrogen to hydrogen repulsion which is very sharp (the interaction

$$\frac{dG_{ex}}{d\rho_{gas}} \rho_{gas} = -V_{film} \tag{5}$$

This high-pressure regime where $\rho_{film} \approx \rho_{film,sat}$ is, however, extremely difficult to reach at room temperature for weakly adsorbing gases such as hydrogen. For example, even at 100 bar the excess adsorption is still growing, and no maximum is even observed (Fig. 4). One possibility is to extrapolate to the high-pressure/high-density regime using the Ono-Kondo model [57,58]:

$$G_{ex} = 2a \left( \frac{1 - \rho_{film,sat}}{\rho_{gas,sat} - 1} \right) - e^{r_{gas}/RT} \tag{6}$$

where $a$ is a scaling factor, $\rho_{film,sat}$ is the saturated adsorbed film density, $e_{s}$ is the binding energy of the gas-solid interaction, and $R$ is the ideal gas constant. It seems unlikely that the relatively narrow range of $\rho_{gas}$ accessible at room temperature would yield a trustworthy fit.

However, we have observed that the saturation density $\rho_{film,sat}$ is quite robust across temperatures and different samples. Figs. 7 and 8 show gravimetric excess adsorption isotherms measured using the Hiden HTP1-V instrument in a broad variety of conditions. This instrument, while only capable of using samples <1 cm$^3$, can span a broader range of temperatures (77–400 K) and pressures (0–200 bar) than the 10LSS. This capability allows it to reach the high gas density regime, where the adsorbed film becomes saturated and the excess adsorption isotherms exhibit a linear decay with the gas density (Eqs. (5) and (6)). Fig. 7 (a) shows adsorption isotherms for a variety of activated carbons including powders, monoliths and polymer-based materials at 77 K. Donhke et al. [68] have shown that, in this regime, the saturated adsorbed film volume is given by the slope $V_{film} = dG_{ex}/d\rho_{gas}$, and the extrapolation to where the line crosses the abscissa ($G_{ex} = 0$) provides a good estimate for the saturated film density, $\rho_{film,sat}$. It is remarkable that in all samples, the estimation of $\rho_{film,sat}$ (97–107 g/L) is higher than that of liquid H2 (71 g/L) and is quite independent of the sample specific surface area, see Fig. 7 (b) [66,68,69]. Additionally, the almost linear relation between $V_{film}$ and specific surface area, in Fig. 7 (c), indicates a common film thickness $t_{film} = V_{film}/S_{BET} \approx 3$ Å which is significantly lower than the typical pore sizes $> 7$ Å. Across a wide range of temperatures (77–173 K), the estimation of $\rho_{film,sat}$ (100–112 g/L) on BR-0311 is also higher than that of liquid H2 (71 g/L) and is quite independent of temperature, see Fig. 8 (b) [68,69]. Additionally, $V_{film}$ tends to decrease with increasing temperature, see Fig. 8 (c) which, as an aside, is similar to what was observed with methane as temperatures increase [70].

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potential rises very abruptly at small distances). This determination quite useful for future developments.

Conversely, \( V_{\text{film}} \) is seen to decrease with increasing temperature. We speculate that the reason for this behavior is that at higher temperatures, the adsorption occurs only in the deepest binding sites, normally associated with narrower pores (whereas at lower temperatures the adsorbate gas would have access to more binding sites). Fig. 9 illustrates this.
idea: more pore sizes contribute to the overall $V_{\text{film}}$ as temperature decreases.

Based on these results, we make the assumption that these values of $p_{\text{film,sat}}$ remain valid at higher temperatures, at least as a first order approximation. This adds one important fixed point to the isotherm ($G_{\text{ex}}(p_{\text{film,sat}}) = 0$, Fig. 6). Only the slope $dG_{\text{ex}}/dp_{\text{ex}}$ at $p_{\text{ex}} = p_{\text{film,sat}}$ is important in what follows. For the calculations that follow, we chose $p_{\text{film,sat}} = 100 \pm 20$ g/L (Figs. 7 and 8). The and error assumed for $p_{\text{film,sat}}$ is estimated from the (i) error estimates of the fitting parameters of the Ono-Kondo model for $G_{\text{ex}}(p_{\text{gas}})$ in Figs. 7 and 8, (ii) the dispersion of values of $p_{\text{film,sat}}$ for different samples, and (iii) the dispersion of values of $p_{\text{film,sat}}$ for sample BR-0311 at different temperatures (neglecting a possible small trend in $p_{\text{film,sat}}(T)$). Calculating the slope of the Ono-Kondo fit in the high gas density regime then yields the volume of the adsorbed film $V_{\text{film}}$ [59,60].

These assumptions result in a good fit to the data (Table 2) that shows a reasonable extrapolated local maximum and high gas density regime (Fig. 6). With the Ono-Kondo fit described above, $V_{\text{film}}$ can be calculated from the slope of the high gas density regime (Eq. (5)).

Interestingly, for BR-0311 the calculated $V_{\text{film}}$ (Table 2) are only ~12% of $V_{\text{pore}}$ (1.45 cm$^3$/g), at cryogenic temperatures (Fig. 8) $V_{\text{film}} = 0.58$ cm$^3$/g (~40% of $V_{\text{pore}}$). The uncertainty in the determination of $V_{\text{film}}$ predominantly arises from the conservatively estimated uncertainty range for $p_{\text{film,sat}} = 100 \pm 20$ g/L (Figs. 7 and 8).

Using this determination of $V_{\text{film}}$ the absolute adsorption isotherms for 273 and 296 K can be calculated (Eq. (4)) and are shown in Fig. 10 (the uncertainty of $G_{\text{abs}}$ arises predominantly from that of $V_{\text{film}}$, see Eq. (4)) along with fits to the Modified Redlich-Peterson model (MRP with $R^2 > 0.9999$) [61]:

$$G_{\text{abs}} = \frac{a(bP)^{1-c}}{1 + (bP)^{1-c}}$$  \hspace{1cm} (7)

These fits are useful to interpolate between experimental points and determine points of constant coverage at the two temperatures in the Clausius-Clapeyron relation (Eq. (3)) [51]. The resulting enthalpy of adsorption $\Delta H(P)$ is shown in Fig. 11; for comparison, a cryogenic temperature determination of $\Delta H$ is also shown.

In Fig. 11 (b), three different $V_{\text{film}}$ assumptions were used to determine $G_{\text{abs}}$ and to calculate the enthalpy of adsorption. For $V_{\text{film}} = 0$ ($G_{\text{abs}} = G_{\text{ex}}$), this leads to a larger enthalpy of adsorption (9 kJ/mol) and an unphysical increase at larger coverage [51] (as discussed, at larger coverage shallower sites should be filled, so for heterogeneous samples $\Delta H$ should decrease with coverage). The assumption $V_{\text{film}} = V_{\text{pore}}$ ($G_{\text{abs}} = G_{\text{sat}}$, see Appendix A) leads to an enthalpy of adsorption that is significantly smaller (6 kJ/mol). Since these too approximations are the most extreme assumptions regarding the $V_{\text{film}}$, an upper and lower bound are set on the enthalpy of adsorption. This narrows the possible values of the enthalpy of adsorption to a 3 kJ/mol range, a 30–50% error.

Using our $V_{\text{film}}$ estimate yields a relatively constant $\Delta H = 8.3 \pm 0.4$ kJ/mol at low coverage, and $\Delta H = 8.3 \pm 0.8$ kJ/mol at high coverage in the 273–296 K range (the error is

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**Table 2** – Parameter $a$ and $E_a$ from the Ono-Kondo fits and the calculated adsorbed film volume and ratio to total pore volume at 296 and 273 K for sample BR-0311 resulting from $p_{\text{film,sat}} = 100 \pm 20$ g/L.

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$A$</th>
<th>$E_a$ (kJ/mol)</th>
<th>$R^2$</th>
<th>$V_{\text{film}}$ (cm$^3$/g)</th>
<th>$V_{\text{film}}/V_{\text{pore}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>10.5</td>
<td>$0.6 \pm 0.6$</td>
<td>0.99993</td>
<td>0.17 $\pm 0.05$</td>
<td>0.12</td>
</tr>
<tr>
<td>273</td>
<td>10.6</td>
<td>$0.6 \pm 0.6$</td>
<td>0.99985</td>
<td>0.18 $\pm 0.05$</td>
<td>0.12</td>
</tr>
</tbody>
</table>

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**Fig. 9** – Illustration of the decrease of $V_{\text{film}}$ with increase of temperature. At lower temperature narrow and wide pores contribute to the adsorption; at higher temperatures only the narrower pores do.

**Fig. 10** – Absolute adsorption isotherms $G_{\text{abs}}(P)$ for BR-0311 using the calculated $V_{\text{film}}$ (Eq. (5)), with the accompanying Modified Redlich-Peterson fit (Eq. (7)) [61]. Error bars are predominantly due to the uncertainty in $V_{\text{film}}$. 

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Summary and conclusions

We developed a new methodology for determining the enthalpy of adsorption $\Delta H$ for hydrogen on activated carbon at room temperature. The methodology is based on (i) measuring two high-quality ca. room temperature adsorption isotherms, (ii) calculating the absolute adsorption isotherms with the aid of cryogenic estimations of the adsorbed film volume, (iii) two high-quality ca. room temperature adsorption isotherms, and (iv) calculating the absolute adsorption isotherms with the aid of cryogenic estimations of the adsorbed film volume.

The results of our methodology can be compared to other methods that either neglect or overestimate the uncertainties in $G_{abs}$ (Fig. 10). This is extremely close to the values calculated at 77 and 87 K of 8.2 kJ/mol at low coverage. This demonstrates how the high temperature $\Delta H$ corresponds to the low-coverage values at low temperatures. This is because at higher temperature, only the sites with the deepest potentials are populated (these deep potential sites are the $\approx$8 kJ/mol wells, at cryogenic temperatures, the high binding energy sites are occupied first at low coverage and then more shallow potential sites down to 5 kJ/mol become occupied). For adsorption onto a substrate without localized binding (i.e., $H_2$ molecules are free to move without the cost or effort of cryogenic refrigeration or very large pressures (a determination $G_{film,sat}$ would be required for other adsorbates).

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Appendix A. Engineering adsorption characteristics of interest

Additional quantities of interest, especially for engineering metrics, are the gravimetric and volumetric storage capacity. They can be calculated from excess adsorption and porosity measurements. Gravimetric storage capacity is defined as the total amount of adsorbate gas stored per mass of adsorbent. It can be calculated as

$$G_{ex} = G_{ex} + \frac{\rho_{gas} V_{void}}{m_s} = G_{ex} + \frac{\rho_{gas}}{m_s} \phi V_{system} = G_{ex} + \frac{\rho_{gas}}{\rho_{sat}} (\phi^{-1} - 1)^{-1},$$

(8)

where $V_{void}$ is total void volume of the system which is equal to the total volume available to the adsorbate gas. In the second expression we used $V_{void} = \phi V_{system}$ in order to define gravimetric storage capacity in terms of the porosity (see Table 3). The last expression shows gravimetric storage capacity in terms of the porosity.
The void space between individual grains of adsorbent material needs to be accounted for in a tank system [62]. The packing fraction of a system depends on the amount of intergranular void space present [34,63,64]. The volumetric storage capacity is defined as the total amount of adsorbate gas in the system normalized to the system volume. Since the total mass of gas stored in the system is the same as in the calculation of gravimetric storage capacity, one only needs to multiply by the density of the system to convert to volumetric storage capacity. Therefore, volumetric storage capacity can be calculated by Ref. [65].

\[ V_{st} = G_{ex} + \rho_{gas} f \]

where \( V_{st} \) and \( G_{st} \) are related through several factors including porosity and excess adsorption. Fig. 12 demonstrates the possible variance in storage capacities for activated carbon samples that have a typical \( \rho_{skeletal} \approx 2.0 \text{ g/cm}^3 \).

Remarkably, both gravimetric and volumetric storage capacities values measured on the large 3 kg sample in the 10LSS agree within 1% to the values measured on the ~300 mg samples in the Hiden instrument across all pressures, see Fig. 13. This demonstrates that despite the amorphous structure of these carbon samples, they are scalable (by a factor of 10,000) and provide consistent structural and storage performance results [64]. Further detail about the 10LSS can be found in our previous work [66,67] and the work done by Rash et al. [34].

**Appendix B. Difference between the enthalpy of adsorption and the adsorption binding energy**

Even though they are different, often the enthalpy of adsorption and the adsorption are used interchangeably in the literature, as they are comparable measures of the interaction between the adsorbate and adsorbent. Given the difference between \( \Delta H = 8.3 \pm 0.1 \text{ kJ/mol calculated (Sec. Results and discussion)} \) and \( E_B = 5.0 \pm 0.6 \text{ kJ/mol estimated in the Ono-Kondo fit (Table 2)} \), it is worth to clarify the possible differences between the two. Let us focus on the enthalpy of the gas phase first (per mol):

**Table 3 – Storage metrics for the monolith sample at 296 and 273 K measured on the 10LSS at 100 bar: gravimetric excess, gravimetric storage, volumetric storage, and total mass of H\(_2\) stored.**

<table>
<thead>
<tr>
<th>T (K)</th>
<th>( G_{ex} ) (g/kg)</th>
<th>( G_{st} ) (g/kg)</th>
<th>( V_{st} ) (g/L)</th>
<th>Mass ( H_2 ) stored (g)</th>
<th>( V_{st}/\rho_{gas} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>6.6</td>
<td>17</td>
<td>9.2</td>
<td>49</td>
<td>1.2</td>
</tr>
<tr>
<td>273</td>
<td>8.0</td>
<td>19</td>
<td>10.4</td>
<td>55</td>
<td>1.3</td>
</tr>
</tbody>
</table>

**Fig. 12 – Volumetric (\( V_{st} \)) vs. gravimetric (\( G_{st} \)) storage capacities, with curves of constant excess adsorption (\( G_{ex} \)) and constant porosity (\( \phi \)). Reproduced from Ref. [66]. Our sample BR-0311 is highlighted.**
\[ H_{\text{gas}} = (E) + PV = \frac{(3+p)RT}{2} + RT, \]  
where \( p = 0, 2 \) for monatomic, diatomic molecules, and we have assumed that vibrational degrees of freedom are heavily quantized and the ideal gas law is satisfied. If we assume that the adsorbed volume is much smaller than that for the gas, \( H_{\text{ads}} \approx (E) \), and consider the adsorption potential as a well of depth \( U_{\text{ads}} \) where particles are confined by a harmonic potential in \( d = 1, 2, \) or 3 dimensions with frequencies \( \nu_i \) (and are free to move in the remainder 3 - d dimensions) \[ \text{then} \]

\[ H_{\text{ads}} = (E) = -U_{\text{ads}} + RT \sum_{i=1}^{d} \frac{(\hbar \nu_i/2k_B T)^2}{\tanh(\hbar \nu_i /2k_B T)} \frac{3 - d + p}{2} \]  
where \( h \) is Planck's constant and the quantization of energy levels of the harmonic oscillators was explicitly considered. We also assume that the rotational degrees of freedom are not significantly affected by the adsorption \[71,72\]. We thus obtain:

\[ \Delta H = H_{\text{gas}} - H_{\text{ads}} = U_{\text{ads}} + \frac{(d+2)RT}{2} - RT \sum_{i=1}^{d} \frac{(\hbar \nu_i/2k_B T)^2}{\tanh(\hbar \nu_i /2k_B T)} \]  
We now consider the following scenarios (see Ref. \[8\] for more details).

a) **Mobile adsorption** (particles are free to move in the xy plane, \( d = 1 \)) in the classical limit \( (k_B T \gg \hbar \nu) \):

\[ \Delta H = U_{\text{ads}} + \frac{RT}{2} \]

b) **Mobile adsorption** (particles are free to move in the xy plane, \( d = 1 \)) in the quantum limit \( (k_B T \ll \hbar \nu) \):

\[ \Delta H = \left( U_{\text{ads}} - N_{\text{A}} \frac{\hbar \nu}{2} \right) + \frac{3RT}{2} = E_0 + \frac{3RT}{2} \]

where in the last term we considered the fact that the true binding energy is shifted by the zero-point energy of the oscillators \( (N_{\text{A}} \text{ normalizes the oscillator energy from per particle to per mol}) \).

c) **Localized adsorption** (particles are tied to local adsorption sites, \( d = 3 \)) in the classical limit \( (k_B T \gg \hbar \nu) \):

\[ \Delta H = U_{\text{ads}} - \frac{RT}{2} \]

d) **Localized adsorption** (particles are tied to local adsorption sites, \( d = 3 \)) in the quantum limit \( (k_B T \ll \hbar \nu) \):

\[ \Delta H = \left( U_{\text{ads}} - N_{\text{A}} \frac{3\hbar \nu}{2} \right) + \frac{5RT}{2} = E_0 + \frac{5RT}{2} \]

Identical results may be obtained using the Clausius-Clapeyron equation for \( \Delta H \) and a Langmuir adsorption model using localized/mobile Henry's law constants as in Ref. \[8\].

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