

Adsorbent density impact on gas storage capacities

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Abstract

In the literature, different approaches, terminologies, concepts and equations are used for calculating gas storage capacities. Very often, these approaches are not well defined, used and/or determined, giving rise to significant misconceptions. Even more, some of these approaches, very much associated with the type of adsorbent material used (e.g., porous carbons or new materials such as COFs and MOFs), impede a suitable comparison of their performances for gas storage applications. We review and present the set of equations used to assess the total storage capacity for which, contrarily to the absolute adsorption assessment, all its experimental variables can be determined experimentally without assumptions, ensuring the comparison of different porous storage materials for practical application. These material-based total storage capacities are calculated by taking into account the excess adsorption, the bulk density (ρ_{bulk}) and the true density (ρ_{true}) of the adsorbent. The impact of the material densities on the results are investigated for an exemplary hydrogen isotherm obtained at room temperature and up

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to 20 MPa. It turns out that the total storage capacity on a volumetric basis, which increases with both, ρ_{bulk} and ρ_{true} , is the most appropriate tool for comparing the performance of storage materials. However, the use of the total storage capacities on a gravimetric basis cannot be recommended, because low material bulk densities could lead to unrealistically high gravimetric values.

Keywords: Physisorption, High pressure hydrogen storage, Supercritical gas adsorption, Activated carbons, Metal-organic frameworks (MOF)

1. Introduction and background

Porous materials like activated or templated carbons [1–4], metal-organic frameworks (MOFs) [5, 6], covalent organic frameworks (COFs) [7], etc. are interesting candidates for gas storage application [8–10]. In the case of supercritical gases, the adsorbed phase cannot condensate, presenting a density gradient inside the Gibbs’ interface [11–13]. This is particularly important for supercritical gases with low molecular weight and relatively weak gas-solid interactions such as hydrogen [14]. For the storage of such gases, the sole use of the excess adsorption amount may not be appropriate, because it does not take into account the contribution of the compressed phase to the total capacity [14–17]. Especially at relatively high pressures and temperatures, a significant amount of gas is stored by compression inside the adsorbent [14–17]. Thus, ways and means need to be found in order to characterize a porous material regarding the total amount of gas which can be stored under practical conditions, i.e. if it is filled into a confined storage volume, and taking into account both, the adsorption and the compression

of the gas inside the void space [14, 16]. Currently, different concepts are used in the literature for calculating storage capacities of adsorbents, some of them being misleading. This problem also affects other storage materials in which the gas is chemically bound [18]. In the following, we present a set of relatively simple equations for calculating the excess adsorption amounts, as well as the total storage capacities on both, gravimetric and volumetric basis. These equations are applied to high pressure hydrogen adsorption isotherms. Furthermore, it is investigated which impact the use of different material densities has on the results.

In an adsorption system, the gas molecules can reside at different locations. The schematic diagram in Figure 1 plots the adsorbate density over the distance from the adsorbent, showing the different phases. The α phase corresponds to the density of the adsorbed *surface excess*, while the β and γ phases correspond to the density of the gas which is stored due to compression inside the adsorbent's void space, i.e., inside its pores and the inter-particle space, respectively [11]. Initially, the densities of all of the phases increase with increasing pressures. The α phase density tends to a maximum value, but it increases faster than the gas density, and therefore, at some point, the difference between both densities reaches a maximum. In the adsorption isotherm this can be observed as a maximum. From this point on, the gas density continues to increase with pressure, and therefore, the difference between them decreases, which causes a decrease of the excess adsorption amount [13]. With experimental devices only the excess adsorption can be measured [12]. In contrast, the *absolute adsorption*, which is the sum of the α and β phases, increases continuously and does not go through a maxi-

mum. This approach is interesting from a theoretical point of view, because it provides fundamental physical models for supercritical adsorption [17, 19]. Unfortunately, it cannot be obtained experimentally, because the location of the Gibbs' interface, as well as the volume and the density of the adsorbed phase (α phase density) cannot be measured [11, 12]. This disadvantage from a practical point of view, for example for gas storage application, can be well solved by using the *total storage capacity* concept, which is the most reliable value that can be obtained. Being the sum of all of the phases (α , β and γ), it accounts for all of the gas molecules which are present inside the system and, thus, the maximum amount of molecules which is available from it.

2. Experimental

In order to study the given equations and demonstrate their application, experimental data obtained for activated carbon fibers (ACF) are used in this study as an example. These ACF were obtained by chemical activation of coal-tar pitch fibers (provided by Osaka Gas Co., Ltd, Osaka, Japan). Chemical activation was carried out in a chamber furnace and under nitrogen flow. For their activation, the carbon fibers were mixed with potassium hydroxide, using a KOH/fiber ratio of 6/1. The mixture was heated with a rate of 5 K min^{-1} up to a maximum temperature of 1023 K which was kept constant for 75 minutes. Afterwards, the furnace was cooled down by convection. After their activation, the ACF were repeatedly washed (first in 5 M solution of hydrochloric acid, and then in distilled water) and vacuum filtered. Finally, the washed ACF were dried at 383 K.

Subatmospheric adsorption isotherms (N_2 at 77 K, and CO_2 at 273 K) of

the samples, degassed at 523 K under vacuum for 4 hours, were performed in a Quantachrome Autosorb. From the obtained data, the apparent BET surface area was calculated, as well as the total micropore volume ($V_{DR}(N_2)$), and the volume of narrow micropores < 0.7 nm ($V_{DR}(CO_2)$) by using the Dubinin-Radushkevich equation.

For H_2 adsorption measurements, gas of 5.0 purity (99.999 %) was used. Previous to each hydrogen adsorption measurement, around 500 mg of sample were degassed at 423 K for 4 hours under vacuum. H_2 adsorption measurements at 77 K were performed in a high-pressure device (DMT GmbH & Co. KG with Sartorius 4406 microbalance). The results were corrected, in order to account for the buoyancy of the balance parts and the sample. At 298 K, H_2 isotherms were measured in a volumetric device, designed at University of Alicante. The free volume was determined with helium, and the device was regularly checked for leaks.

Packing densities were measured in a mechanical press, by introducing around 500 mg of sample into a cylindrical steel mould, and by applying a mechanical pressure of 73.9 MPa on it. The volume occupied by the sample was evaluated, taking into account a reference measurement without sample.

True densities were measured in a Micromeritics Accupyc 1330 pycnometer. Before every measurement the samples were degassed at 393 K into vacuum for at least 4 hours, and the device was calibrated with steel balls of perfectly known volumes. Sets of 10 helium displacement measurements were performed and repeated several times, until the average value of each set remained constant.

Further details on the synthesis and characterization of the investigated

sample can be found elsewhere [16].

3. Equations

In the following, it will be shown how the total storage capacity can be obtained from the excess adsorption, by simple use of the gas density and the adsorbent densities.

The data output of an adsorption device typically delivers the excess adsorption as moles per gram of adsorbent ($\frac{n_{exc}}{m}$). In order to present this value as gravimetric excess adsorption amount in wt.% ($x_{exc,grav}$), Equation 1 is applied.

$$x_{exc,grav} = 100 \cdot \frac{n_{exc} \cdot M}{n_{exc} \cdot M + m} \quad (1)$$

Thereby, n_{exc} is the number of moles of gas molecules which are adsorbed in excess, m is the adsorbent mass in g, and M is the molar mass of the adsorbed molecule (i.e., 2.01588 g mol⁻¹ in the case of H₂). The volumetric excess adsorption ($x_{exc,vol}$) in g l⁻¹ can be calculated by means of Equation 2 if the adsorbent density (ρ_{bulk}) is known.

$$x_{exc,vol} = \frac{n_{exc}}{m} \cdot M \cdot \rho_{bulk} \quad (2)$$

In order to calculate the total volumetric storage capacity ($x_{tot,vol}$), which takes into account the gas compression inside the void space, the following equation is applied.

$$x_{tot,vol} = x_{exc,vol} + \rho_{gas} \cdot C \quad (3)$$

Thereby, ρ_{gas} is the density of the gas due to compression under the given thermophysical conditions, and C is the void space contribution that includes the volume of the porous structure in which the adsorption takes place, as well as the inter-particle space. This void space contribution can be determined by the following formula [14].

$$C = \frac{V_2 - V_1}{V_2} = 1 - \frac{V_1}{V_2} \quad (4)$$

Herein, V_1 is the volume of the atoms of the adsorbent, and V_2 is the bulk volume occupied by the adsorbent sample. With $\rho_{true} = \frac{m}{V_1}$ and $\rho_{bulk} = \frac{m}{V_2}$ Equation 4 can be converted to:

$$C = 1 - \frac{\rho_{bulk}}{\rho_{true}} \quad (5)$$

With the aid of the total volumetric storage capacity and the bulk density of the adsorbent, the total storage capacity on a gravimetric basis can be calculated by Equation 6.

$$x_{tot,grav} = 100 \cdot \frac{x_{tot,vol}}{x_{tot,vol} + \rho_{bulk}} \quad (6)$$

For the calculation of the volumetric excess adsorption and the total storage amounts, the use of realistic material densities is essential. The true density (ρ_{true}), that refers to the volume which is occupied by the atoms of the adsorbent material, has to be measured. For activated carbon materials, a theoretical maximum value would be the density of graphite. However, experimentally, the true density should be obtained with a pycnometer, measuring the expansion of a gas with very weak interaction potential. Typically,

helium is used for this purpose, assuming that it penetrates the porous structure of the adsorbent without being adsorbed, although it has been reported that for some adsorbents the interaction with helium may not be negligible [12, 17, 20]. For the measurement of the bulk density (ρ_{bulk}), which refers to the volume that is occupied by the sample inside a storage tank, different methods can be used. One possibility is to use the tap density of the adsorbent [21]. However, it is expected that, for practical storage purpose, the adsorbent in a tank device would be compacted in order to increase its density. Hence, the use of the packing density of the adsorbent, measured under mechanical compression, is more advisable. Thereby, it has to be taken into account to which point mechanical pressure could alter the porosity of the adsorbent. While activated carbon materials are relatively resistant in this sense, the porous structure of MOFs is very susceptible to external forces [22–24].

In the literature, sometimes different approaches for adsorption and storage calculations can be found. Without doubt, the simplest and mostly used concept of gravimetric adsorption excess gives comparable results among most of the authors. However, despite the general agreement among scientists in the field [6, 25–28], an example of a misleading concept is the overestimation of the gravimetric excess adsorption by leaving out the addend $n_{exc} \cdot M$ in the denominator of Equation 1. Thereby, the sample’s weight gain due to the adsorbed gas is disregarded, which leads to “ $g_{adsorbate}/g_{adsorbent}$ ” instead of “wt.%”. However, often the unit “wt.%” is preserved, suggesting higher values [29–31]. For instance, as an example of many published results dealing with MOFs, the frequently cited H₂ maximum adsorption of 7.5 wt.%

for MOF-177 at 77 K [30] translates to a lower value of 7.0 wt.% (or 7.5 g/g). In addition, the volumetric excess densities of MOFs and COFs are often calculated by taking into account their crystal densities [29–31] instead of their bulk (tap or packing) densities, which, unfortunately, are scarcely reported [5, 21, 22, 24, 32, 33]. This practice leads to overestimated volumetric excess adsorption results, because it does not account for the void spaces in-between the particles of the powdered samples, as it has been clearly shown and discussed elsewhere, especially considering that the bulk densities of MOFs and COFs are lower than for activated carbon materials [23, 32, 34].

4. Results and discussion

In the following, the excess adsorption amounts and the total storage capacities are calculated exemplary for hydrogen adsorption on activated carbon fibers (ACF). The sample has a BET surface area of $2259 \text{ m}^2\text{g}^{-1}$, as well as total and narrow micropore volumes $V_{DR}(\text{N}_2)$ of $0.97 \text{ cm}^3\text{g}^{-1}$, and $V_{DR}(\text{CO}_2)$ of $0.71 \text{ cm}^3\text{g}^{-1}$, respectively [16]. For the bulk density of the adsorbent a value of 0.6 g cm^{-3} was used, which corresponds to the packing density of the ACF, measured in a mechanical press by applying a pressure of 74 N mm^{-2} . The true density of 2.2 g cm^{-3} was measured by helium expansion in a pycnometer. Hydrogen adsorption isotherms were measured on this ACF sample at 77 K and up to 4 MPa, as well as at 298 K and up to 20 MPa. In Table 1, the maximum adsorption amounts obtained under these conditions are given in mmol g^{-1} . In addition, the corresponding gravimetric adsorption amounts in wt.% were calculated from these values by applying Equation 1. The volumetric adsorption amounts, as well as the

total storage capacities on volumetric and gravimetric basis were calculated from Equations 2, 3, and 6, respectively.

The influence of the temperature on adsorption and compression is discussed in the following. In Figure 2 the hydrogen isotherms of the ACF sample are shown for 77 K and up to 4 MPa (Figure 2(a)), and for 298 K and up to 20 MPa (Figure 2(b)). For each temperature, the adsorption isotherms are shown on a volumetric basis, together with the compressed amounts of gas inside the void space, as well as the total storage amounts. In Figure 2(a), it can be observed that, for cryogenic temperatures of 77 K, the excess adsorption isotherm achieves a value around 27 g l^{-1} at a pressure of 4 MPa. The compressed hydrogen in the void space reaches a lower value close to 10 g l^{-1} . However, due to its contribution, the total storage capacity is higher than the adsorption isotherm, reaching a maximum value of 34 g l^{-1} . At 298 K the picture changes (see Figure 2(b)). Thus, the compressed hydrogen in the void space reaches close to 14 g l^{-1} which is more than twice of the adsorbed amount (6 g l^{-1}). Thanks to its contribution, the total storage capacity reaches a high value of more than 16 g l^{-1} which is significantly higher than for adsorption only. The findings from Figure 2 underscore the importance of the total storage capacity. It shows that the contribution of each phase to the total storage is highly dependent on the thermophysical boundary conditions, namely temperature and pressure. Thus, for high temperatures and pressures, the compression contribution gains importance, while at 77 K the contribution of excess adsorption is more important.

Especially at room temperature, a high contribution to the total storage capacity of the compressed H_2 in relation to the adsorption can be observed.

In order to further study the impact that the material densities have on the resulting hydrogen isotherms under room temperature conditions, the following theoretical calculations are done: In Figure 3, the true densities are varied between 1.2 and 2.2 g cm⁻³, keeping constant the bulk density of 0.6 g cm⁻³. In the diagrams, the adsorption isotherms and the total storage capacities are shown, which were calculated by using the mentioned range of density values. In Figure 3(a), the isotherms are represented on a volumetric basis, and in Figure 3(b) on a gravimetric basis. In the case of the volumetric representation, also the thermophysical density of hydrogen at 298 K ($\rho_{H_2,298K}$) is included [35]. It can be seen that, independently of expressing the results in a volumetric or a gravimetric way, the total storage capacity is much higher than the excess adsorption. In both diagrams, it can be observed that the excess adsorption isotherms are not affected by the utilization of different true densities, because they are not involved in the calculations (see Equations 1 and 2). On the other hand, the total storage capacity is dependent on the true density of the material. Thus, higher total storage capacities on both, volumetric as well as gravimetric basis, are obtained for increased true densities. When the true density increases, the volume occupied by the atoms of the material (V_1) decreases, which means that the void space (C) increases (see Equations 4 and 5), and this implies a higher contribution of the thermophysical density of the gas (ρ_{gas}) to the total volumetric storage capacity (Equation 3). In Figure 3(a), the maximum total storage capacity at 20 MPa is 16 g l⁻¹, a value clearly superior to the corresponding $\rho_{H_2,298K}$ value (14 g l⁻¹). On the other hand, at high pressures, low ρ_{true} values lead to H₂ storage capacities which are below

$\rho_{H_2,298K}$. Furthermore, it can be observed that for incrementally increasing true densities, the distances between the isotherms subsequently decrease. This can be explained by the void space contribution (C), which tends to 1 when the true density increases, but not linearly (see Equation 5). Thus, variations of relatively high ρ_{true} values, for example around 2.2 g cm^{-3} , have less impact on the total storage capacity than similar variations of the lower true densities, e.g. around 1.2 g cm^{-3} . In agreement with Equations 1 and 2, the results shown in Figure 3 reveal that the excess adsorption on gravimetric and volumetric basis do not depend on the true density of the adsorbent. Contrarily, the total H_2 storage depends very much on the true density of the used adsorbent. From these results that demonstrate the importance of using correct true density values for storage capacity calculations, it has to be recommended to use measured true densities for each studied material, instead of using approximated values.

In Figure 4, a fixed true density value of 2.2 g cm^{-3} is used, which is the actual true density measured by helium pycnometry on this ACF, and different bulk densities between 0.2 and 1 g cm^{-3} are assumed. A maximum of 1 g cm^{-3} was chosen, because such value can be regarded as a realistic state-of-the-art maximum density for porous carbon materials. Thus, recently adsorption of H_2 , CH_4 , and CO_2 on monoliths with such high density has been reported [4]. Similar to the representation in Figure 3, the adsorption isotherms and the total storage capacities are shown on a volumetric basis (see Figure 4(a)), and on a gravimetric basis (Figure 4(b)). As expected from Equation 1, the gravimetric excess adsorption value in Figure 4(b) is independent from the bulk density. In Figure 4(a), it can be observed that

on a volumetric basis both, hydrogen excess adsorption, as well as the total H₂ storage capacity, are considerably affected by the bulk density, increasing for both cases with the bulk densities. Nevertheless, the impact of the bulk density is much stronger in the case of the volumetric excess adsorption, than for the volumetric total H₂ storage, and a wide range of maximum H₂ adsorption capacities between 2 and 9.5 g cm⁻³ is covered for the studied scope of bulk densities. This highlights the importance of using realistic bulk density values in Equation 2. The use of higher density values (e.g., the crystal density, which does not account for the inter-particle space) like it is done in other works, leads to overestimated values and lacks any practical significance [32]. In relation to the much weaker effect of the bulk density on the total storage capacity, Figure 4(a) shows a range of maximum values between 14.5 and 17 g cm⁻³, and at no point H₂ storage capacities lower than $\rho_{H_2,298K}$ are obtained. The results emphasize the suitability of Equation 3 for total storage capacity characterization of storage materials. The importance of the material density can be highlighted in the case of very dense activated carbon monoliths ($\rho_{pack} \approx 1$ g cm⁻³), which, despite their moderate porosity (BET surface areas around 1000 m²g⁻¹), reach very high volumetric total H₂ storage capacities as high as 18 g l⁻¹ at 298 K and 20 MPa [4].

Figure 4(b) reveals that, on a gravimetric basis, the bulk density does not have any influence on the adsorbed amount of hydrogen, as it is expected from Equation 1. Thus, the maximum adsorption amount of 0.95 wt.% remains constant for all of the studied bulk densities. In contrast, the total H₂ storage capacity on a gravimetric basis is highly sensitive to the bulk density, *lower* bulk densities resulting in *higher* total H₂ storage capacities,

whereas *higher* bulk densities produce *lower* gravimetric total H₂ storage capacities. It has to be emphasized that this tendency is opposed to all of the other combinations of densities that were investigated. Furthermore, the total gravimetric storage capacity is stronger biased for lower bulk density values. For a realistic bulk density of 0.6 g cm⁻³, the total H₂ capacity reaches a value of 2.6 wt.%, while a very high density of 1 g cm⁻³ results in a significantly lower value of 1.7 wt.%. However, the main problem turns out to be, if too low bulk densities are assumed. This leads to an extreme increase of the total storage capacity. For example, assuming a low bulk density of 0.2 g cm⁻³, the total gravimetric H₂ capacity increases extremely to an unrealistic value of almost 7 wt.%. If, mathematically, the bulk density tends to zero, then the total storage capacity converges towards 100 wt.%. As a thought experiment, one could think of a given tank with a fixed volume, in which the amount of sample is more and more reduced (leading to lower “bulk densities”). The amount of gas in the void space would increase with decreasing amount of sample. If few amount of sample would be left, then most of the gas molecules in the system would be stored by compression in the void space. However, all of these molecules being present in the volume would, misleadingly, still be associated with the few amount of sample.

In order to prevent confusions, it has to be emphasized that all of the terms for gas storage capacities (excess, absolute, or total) that are used here, as well as in the literature, are material-based and not system-based [9, 16, 18]. For practical considerations, and demanded by policy makers, are gravimetric and volumetric storage capacities which take into account the whole tank system (including the tank shell, auxiliary devices, etc.) [36].

Because the system-related tank features are under constant development, the ongoing research on storage materials needs to use the concepts presented here. Taking into account their limitations, they provide the possibility to compare the performance of different kinds of storage materials, the total storage capacity being the most suitable concept for analysing the performance of an adsorbent material inside a confined tank volume.

5. Conclusions

In summary, equations are given for the accurate calculation of the material-based excess and total storage capacities. The formulas provide the possibility to compare results among different classes of porous materials, presuming that these are filled inside a confined tank volume. A theoretical study is carried out in order to investigate the impact of the adsorbent density on the results. From the findings, it can be concluded that the total storage capacity on a volumetric basis is the most appropriate tool for the characterization of a porous storage material which occupies a given tank volume. In addition to the adsorbed gas phase, it accounts for the compressed gas inside the adsorbent's pores and inside its void space. The compressed gas contributes significantly to the total amount of gas that can be stored by an adsorbent, especially at high temperatures and pressures. It increases for increasing true densities, as well as for increasing bulk densities of the adsorbent material. Contrarily, the use of the total storage capacity on a gravimetric basis cannot be recommended, because very high values would be reached if too low bulk densities would be taken into account for its calculation.

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Table 1: Maximum excess adsorption and total storage capacities on gravimetric and volumetric basis for H₂ adsorption on an ACF sample.

	Units	Eq.	77 K / 4 MPa	298 K / 20 MPa
H ₂ excess	mmol g ⁻¹	—	23.30	4.68
	wt.%	(1)	4.34	0.93
	g l ⁻¹	(2)	27.2	5.7
H ₂ total	g l ⁻¹	(3)	33.7	16.0
	wt.%	(6)	5.32	2.59

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- 4 Excess adsorption isotherms and total storage capacities of H₂ at 298 K and up to 20 MPa on (a) volumetric basis, and (b) gravimetric basis. A fixed true density ρ_{true} of 2.2 g cm⁻³, and a range of bulk densities ρ_{bulk} between 0.2 and 1 g cm⁻³ are used for the calculations. In (a), also the supercritical fluid density $\rho_{H_2,298K}$ is plotted (dashed line). 25

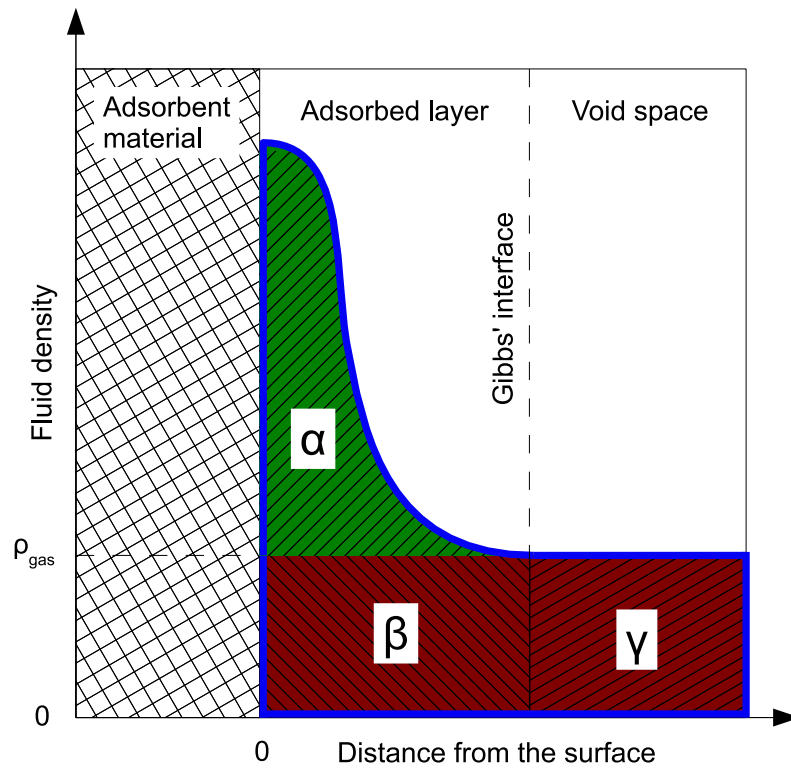
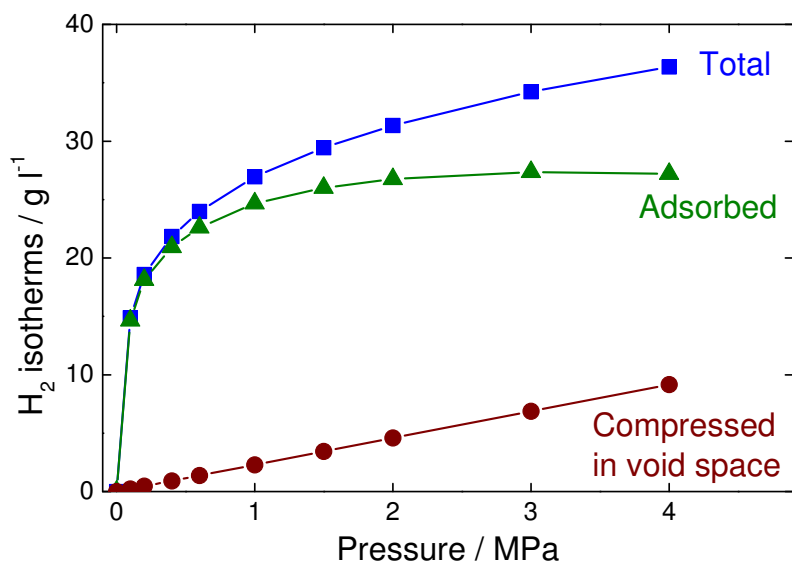
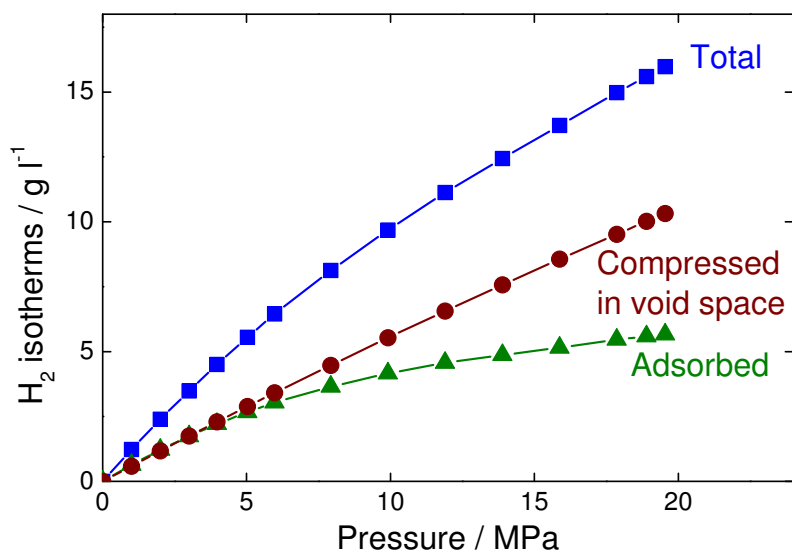


Figure 1: Schematic diagram of the different regions in which the stored gas can reside: Adsorbed surface excess (α), compressed phase in the adsorbed layer (β), compressed phase in the void space (γ).

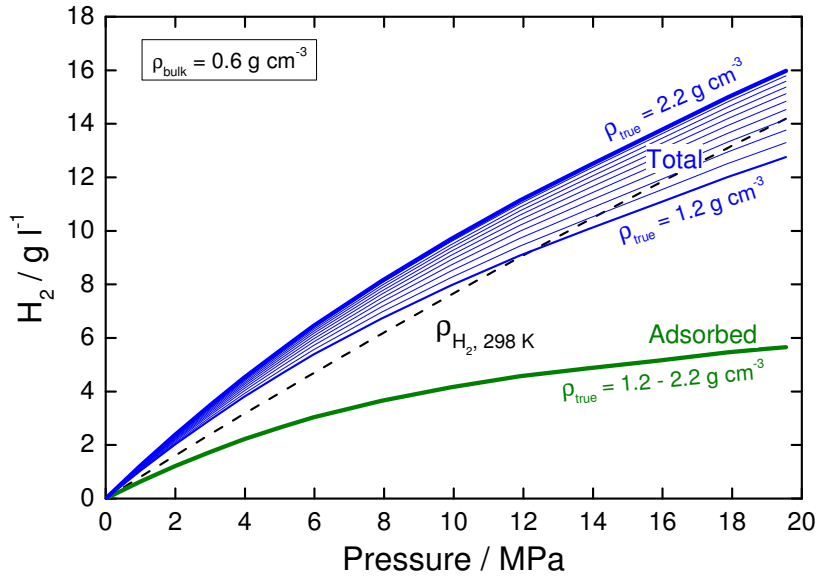


(a) 77 K

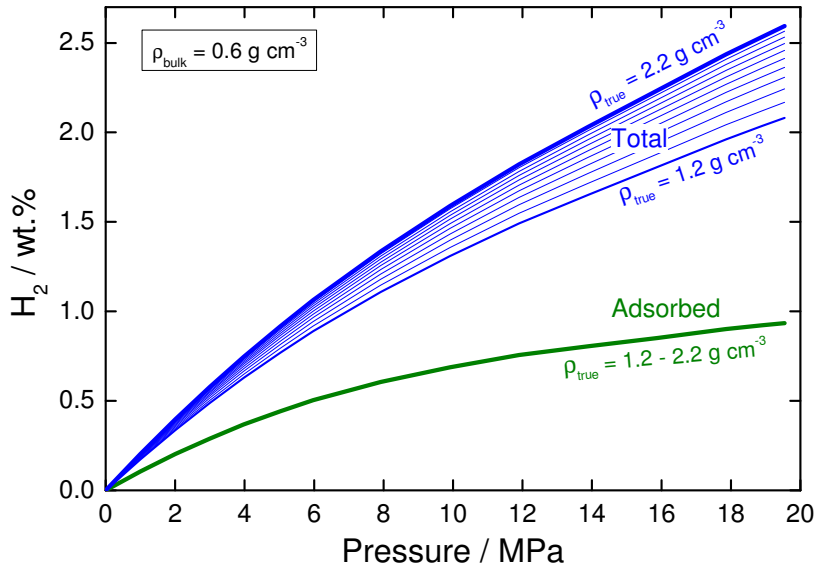


(b) 298 K

Figure 2: Volumetric hydrogen isotherms for an ACF sample at (a) 77 K, and (b) 298 K. In addition to the total storage isotherms, the contributions of the excess adsorption and the compression in the void space are shown.

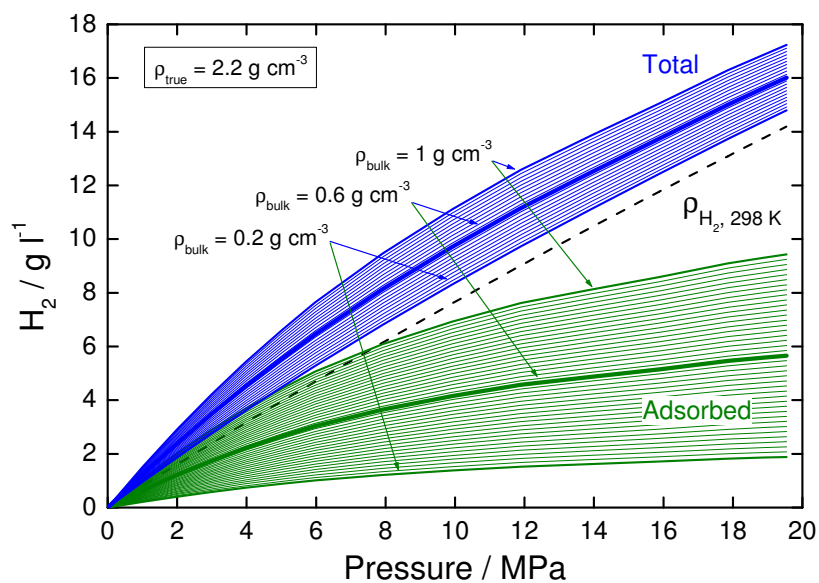


(a) volumetric

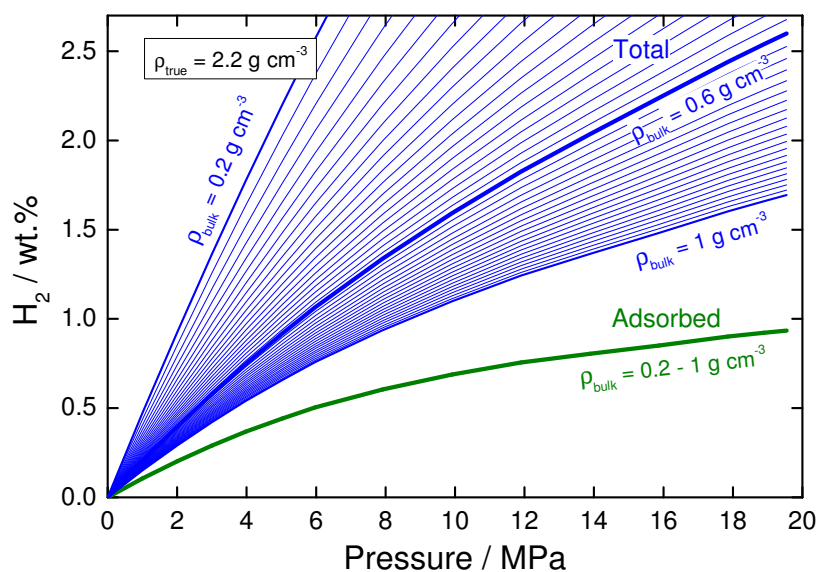


(b) gravimetric

Figure 3: Excess adsorption isotherms and total storage capacities of H₂ at 298 K and up to 20 MPa on (a) volumetric basis, and (b) gravimetric basis. A fixed bulk density $\rho_{\text{bulk}} = 0.6 \text{ g cm}^{-3}$, and a range of true densities ρ_{true} between 1.2 and 2.2 g cm^{-3} are used for the calculations. In (a), also the supercritical fluid density $\rho_{\text{H}_2, 298 \text{ K}}$ is plotted (dashed line).



(a) volumetric



(b) gravimetric

Figure 4: Excess adsorption isotherms and total storage capacities of H_2 at 298 K and up to 20 MPa on (a) volumetric basis, and (b) gravimetric basis. A fixed true density ρ_{true} of 2.2 g cm^{-3} , and a range of bulk densities ρ_{bulk} between 0.2 and 1 g cm^{-3} are used for the calculations. In (a), also the supercritical fluid density $\rho_{H_2, 298K}$ is plotted (dashed line).