



# Surface excess amounts in high-pressure gas adsorption: Issues and benefits



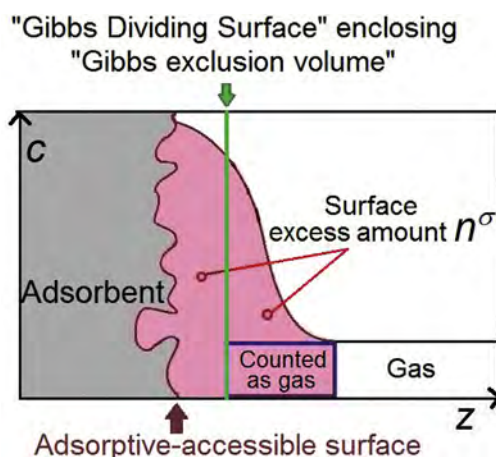
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## HIGHLIGHTS

- The dead volume issue in high pressure gas adsorption is carefully examined.
- The usual Gibbs representation is modified for adsorption by microporous adsorbents.
- The concept of "Gibbs exclusion volume" is proposed for a safe data reporting.
- Case study: how to improve an inter-laboratory comparison of adsorption data.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This paper introduces a calculation procedure aimed at improving the accuracy and meaningfulness of high-pressure gas adsorption data obtained by either adsorption manometry or gravimetry. The procedure is based on the Gibbs model and avoids the usual simplifying assumption that the well-defined Gibbs dividing surface (the GDS) coincides with the ill-defined adsorptive-accessible surface of the microporous adsorbent. Instead, it makes a clear distinction between the two surfaces and introduces the concept of "Gibbs exclusion volume" (i.e. the volume enclosed by the GDS) which is shown to be central in the calculation of the surface excess amount and useful to avoid any confusion with the adsorbent volume. It is shown, in the case of methane adsorption on gas shale, how this procedure avoids introducing the uncertainty due to the dead volume determination in an inter-laboratory comparison. The conditions for a surface excess isotherm to be a useful intermediate step in the assessment of the amount adsorbed are stressed and illustrated.

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## 1. Introduction

It is commonly accepted that both manometric and gravimetric adsorption experiments directly lead to *surface excess amounts*. At the same time, it is considered that the *amount adsorbed* is the

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## Nomenclature

$c^g$	concentration of the gas phase
$M_i$	molar mass of adsorptive “i”
$n$	total amount of adsorptive enclosed in volume $V$
$n^a$	amount adsorbed, i.e. contained by the adsorption space ( $n^a$ also stands for specific surface amount, i.e. per unit mass of adsorbent, depending on the context)
$n^\sigma$	surface excess amount, always relative to a given value of the “Gibbs exclusion volume” $V_{GDS}$ ( $n^\sigma$ also stands for the specific surface amount, i.e. per unit mass of adsorbent, depending on the context)
$\Delta m$	recorded mass change in adsorption gravimetry experiment
$\Delta m^a$	mass adsorbed in adsorption gravimetry experiment
$\rho_i^g$	gas or fluid density of adsorptive “i”
$V$	internal volume of manometric adsorption set-up, with no sample, i.e. bulb volume + dosing volume and pressure transducer ( $v$ if specific, i.e. per unit mass of adsorbent)
$V_i^a$	volume of the adsorption space for adsorptive “i” ( $v_i^a$ if specific, i.e. per unit mass of adsorbent)
$V_i^g$	“dead volume” seen by adsorptive “i”, i.e. volume of the “dead space” available to the gas phase “i” and which is limited by the internal walls of the adsorption manometry set-up and by the outer limit of the adsorption space for adsorptive “i”
$V_i^s$	adsorbent volume inaccessible to adsorptive “i”. ( $v_i^s$ if specific, i.e. per unit mass of adsorbent)
$V_{He}^s$	adsorbent volume inaccessible to helium ( $v_{He}^s$ if specific, i.e. per unit mass of adsorbent)
$V_{GDS}$	“Gibbs exclusion volume”, i.e. volume enclosed by the GDS ( $v_{GDS}$ if specific, i.e. per unit mass of adsorbent)
$V_{Gibbs}^a$	volume of the adsorption space in Gibbs representation (=0)
$V^B, V^C, V^D$	gas volumes represented in Fig. 8 by rectangles B, C and D, respectively
$\Gamma^\sigma$	surface excess concentration $n^\sigma/A$ (where $A$ is the surface area)

quantity needed all at once for practical applications of adsorption (determination of adsorptive capacity, BET area, pore-size distribution. . .) and for its understanding (comparison of adsorption equations between themselves or of experimental data with those assessed by simulation and modeling) [1–3].

Hence, two opposite viewpoints found in the literature. Some are advocating for a systematic presentation of adsorption isotherms in the form of surface excess amounts, even proposing a new classification of isotherms (Donohue and Aranovitch [4]), different from the generally accepted IUPAC classification of isotherms for vapor adsorption (Thommes et al. [5]). The latter isotherms are indeed plotted in amounts adsorbed, i.e. in what is considered to be their final useful form. Going further in the same direction, some authors even raise strong reservations about the use of surface excess amounts in the case of gas adsorption by microporous adsorbents (Serpinskii and Yakubov [6], Tolmachev [7], and, most recently, Myers and Monson [8] in the scope of a detailed thermodynamic treatment).

This is why, the two questions we wish to answer in this paper are (i) is the surface excess presentation of gas adsorption data still useful to address the issues found in the determination of the

amount adsorbed by microporous solids under high pressure and (ii) if yes, under what conditions.

## 2. Issues found in the determination of the amount adsorbed under high pressure

### 2.1. Part of the dead volume in the calculation

The issues we shall consider are mainly found with adsorbents containing micropores (i.e. less than 2 nm wide), which are precisely those of interest in high-pressure adsorption processes. Although our reasoning will be first carried out in the scope of adsorption manometry, we shall see, in a final section, how to extend it to adsorption gravimetry, much used in the high-pressure range.

In gas adsorption, the *amount adsorbed* is defined as the content of the *adsorption space*, the latter including all places where the concentration of the adsorptive is higher than in the bulk of the surrounding gas phase [5]. Incidentally, since we shall stick to this precise definition of the amount adsorbed, we shall not need using clarifying terms like “absolute amount adsorbed” [9] or “total amount adsorbed” [10].

For adsorption of a single gas monitored by adsorption manometry, the calculation of the amount adsorbed  $n^a$  is apparently most simply carried out after:

$$n^a = n - c^g V_i^g \quad (1)$$

where  $n$  is the total amount of gas enclosed in the system and  $c^g$  the final gas concentration in the “dead space” available to adsorptive “i” in its gas phase. This dead space has a volume  $V_i^g$  (the “dead volume”). For the sake of clarity we shall only mention the “dead space” and its “dead volume” for application of Eq. (1). Also, for an easier understanding, the definitions of the symbols used in this paper are listed in the Nomenclature section at the beginning.

Unfortunately, the dead volume is not that easy to determine accurately, so that it is currently considered to be the major source of uncertainty in the calculation of the amount adsorbed [11,5]. Hence, the few comments hereafter.

### 2.2. Definition of the dead volume

The dead volume  $V_i^g$  we need in Eq. (1) to calculate any point of the adsorbed amount isotherm is the volume available to the gas phase, up to the outer limit of the adsorption space:

$$V_i^g = V - (V_i^s + V_i^a) \quad (2)$$

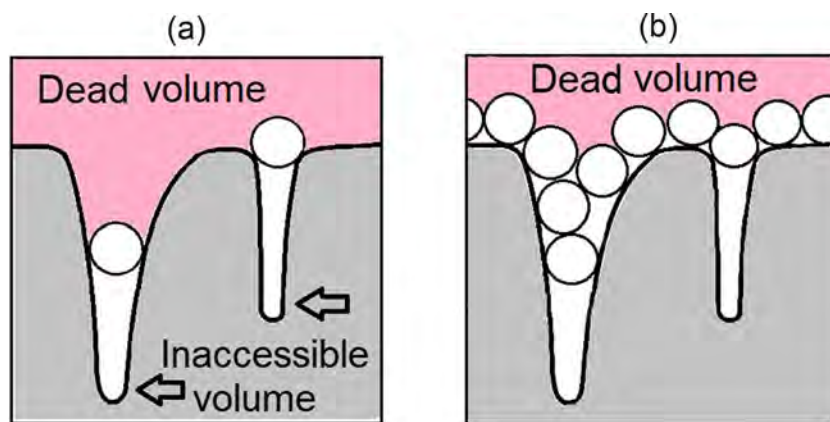
where  $V$  is the sum of the volume of the empty adsorption bulb + the dosing volume up to the membrane of the pressure transducer,  $V_i^s$  is the adsorbent volume inaccessible to the molecules of adsorptive “i” and  $V_i^a$  is the volume of the adsorption space for adsorptive “i”, i.e. the adsorbate volume. Subscript “i” in  $V_i^g$  stresses that the dead volume may depend on the adsorptive.

### 2.3. Change of the dead volume as adsorption proceeds

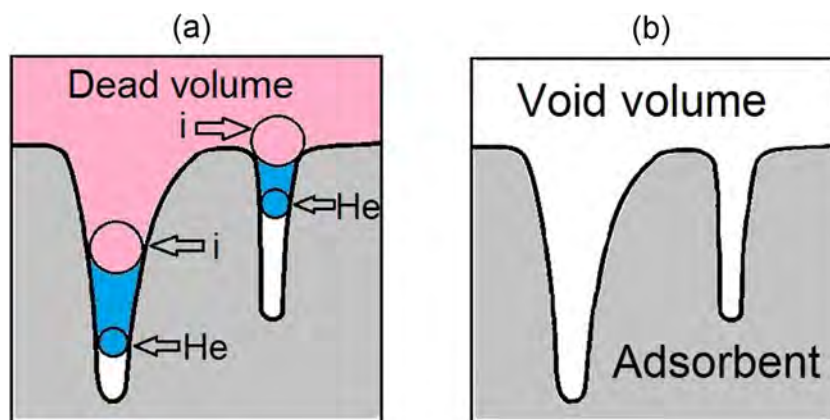
The adsorbate volume  $V_i^a$  logically changes as adsorption proceeds, what has a direct effect on the dead volume, as illustrated in Fig. 1a (corresponding to the onset of adsorption, when the adsorbate volume is minimum and the dead volume maximum) and 1-b (where the adsorption space is larger).

### 2.4. Assessment of the dead volume when the adsorbent is microporous

The usual way for assessing the dead volume is based on expansion of a gas assumed not to adsorb in the conditions chosen for the



**Fig. 1.** Change of dead volume between (a) onset of adsorption and (b) complete micropore filling, as the volume of the adsorption space (made up of the spherical molecules of adsorbate) increases.



**Fig. 2.** Volumes assessed (a) by expansion of helium or gas «i» and (b) from skeletal density of adsorbent.

measurement. Helium is commonly used, though it is well known that helium is prone to adsorption in micropores, then leading to a larger apparent dead volume than expected [12–19], an effect which can be minimized by increasing the measurement temperature [20,21] and which can be taken into account by appropriate procedures [22,17,23]. Nevertheless, even then, and even in the absence of any adsorption, the small size of the helium molecule may allow assessing a larger volume than that available to the adsorptive molecule, as represented in Fig. 3a. In the opposite, it was also suggested not to reject the possibility that helium, being more inert than many adsorptives, could finally assess a smaller volume [19]. These last shortcomings could in principle be avoided by using expansion of the adsorptive itself, at a temperature where adsorption is expected not to occur, but, usually, this condition is even more difficult to fulfill than with helium when the adsorbent is microporous. It is only in simulation studies that the dead volume can be correctly calculated, but attention must then be paid to the definition of the volume inside the pores: it can be either the volume limited by a surface passing through the center of the surface atoms of the adsorbent [20], or the volume that is accessible to the center of the adsorbed molecules [24–26], therefore limited by an “r-distance surface” or, still, the volume limited by the “probe-accessible” surface [5], also known as the “Connolly surface” when the probe is spherical (i.e. the surface drawn by the bottom of a spherical molecule rolling over the van der Waals surface of the adsorbent). The latter probe-accessible volume is the closest to the volume expected to be assessed by a “good experiment” of gas expansion and is the dead volume we are referring to in Eq. (2).

It may also make sense of simply using the “skeletal” density of the adsorbent, either calculated from structural data (in case of

crystalline adsorbents) or measured on a non-porous material of similar composition and state. For microporous materials, the “void volume” then assessed (see Fig. 2b) tends to be larger than the dead volume which is looked for (see Fig. 2a).

We should therefore conclude that, in the case of microporous adsorbents, the evaluation of the dead volume required to derive the amount adsorbed with help of Eq. (1) is not a simple matter and opens the way to personal appreciation and assumptions.

This uncertainty in the dead volume logically results in an uncertainty in the amount adsorbed. Although this uncertainty has been continuously- and reasonably—considered as usually negligible for adsorption of vapors below 1 bar, this is not any more the case for high-pressure adsorption, as well recognized by the scientists in this field and illustrated in Section 4. Fortunately, if we wish to keep the experimental adsorption data with their original accuracy, without spoiling them by any uncertain value for the dead volume, we can draw benefit from the Gibbs model in the way developed hereafter.

### 3. The Gibbs model: representation and requirements

“For the precise measurement of the quantities” Gibbs devised a representation whose principle, when applied to adsorption, can be summarized as follows:

- Imagine a “geometrical surface”, close to the adsorbing surface, with “a precisely determined position” and which will “be called the Dividing surface” (Gibbs [27]) (we call it now the “Gibbs dividing surface” (GDS)).

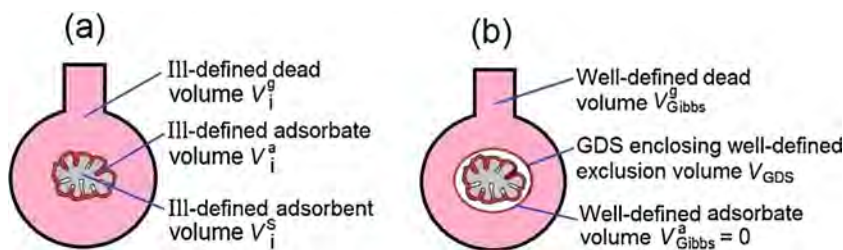


Fig. 3. Adsorption system (a) real and (b) idealized by Gibbs.

- Assume that adsorption takes place on that GDS.
- Also assume, for the sake of a simplified calculation, that the volume  $V^a$  of the adsorption space (i.e. the space in which the concentration of the adsorptive is higher than in the surrounding gas phase) is continuously equal to zero.
- Then call the resulting quantity, i.e. the virtual amount located on the GDS, a “surface excess amount”.

Two types of schemes may help appreciating the meaning and also the relativeness of this concept of surface excess amount.

In a first instance, we can represent the adsorption system as totally enclosed in a container of volume  $V$  as shown in Fig. 3a. This volume  $V$  is equivalent to the volume of the empty adsorption bulb + the dosing volume.

Fig. 3a stresses the uncertainties found in the description of a real system with adsorptive “i”: uncertainties (i) in the dead volume  $V_i^g$  available to “i”, (ii) in the adsorbent volume  $V_i^s$  inaccessible to “i” and (iii) in the adsorbate volume  $V_i^a$ .

Fig. 3b shows the same system, but now in the scope of the Gibbs representation: the adsorbate volume  $V_{Gibbs}^a$  is assumed to be zero, whereas a well-defined GDS (here, a closed surface, whose location is selected by the experimenter) separates the well-defined outer volume of the gas phase from a well-defined inner volume  $V_{GDS}$ . Given that this inner volume plays an essential part in the calculation of the surface excess amount  $n^\sigma$  (see Eq. (3)) it is convenient to give it a name; we shall call it hereafter the “Gibbs exclusion volume” since, by definition and for the sake of the calculation of  $n^\sigma$ , it is assumed to be inaccessible to the adsorptive, with the symbol  $V_{GDS}$  since it is the volume surrounded by the GDS. Now, all volumes are well-defined and so is the resulting surface excess amount  $n^\sigma$  which is easily obtained as:

$$n^\sigma = n - c^g(V - V_{GDS}) \quad (3)$$

where  $n$  is the total amount of adsorptive introduced in the system and  $c^g$  the final experimental concentration of the gas phase. It can be seen, after this equation, that the choice of the GDS location by the experimenter simplifies into the mere choice of a value for  $V_{GDS}$ . We may also notice, from Eq. (3), that the calculation of the surface excess amount can in reality be carried out, with unchanged accu-

racy, whatever the value of the “Gibbs exclusion volume”  $V_{GDS}$ , i.e. whatever the position of the GDS. Since *our sole objective is here to use the surface excess amount as an intermediate step in view of assessing a meaningful amount adsorbed*, we propose to simply drop the original Gibbs constraint of a GDS “in or very near to the surface of discontinuity”. In this way, we also drop the corresponding need of accurately determining the adsorbent volume  $V_i^s$  before evaluating any surface excess amount. Since the evaluation of  $V_i^s$  is delicate and is a source of inaccuracy with microporous adsorbents, we can then avoid spoiling the reported experimental data. In other words, we do not need any more to focus on the validity of the  $V_i^s$  determination but simply on the choice of a well-defined value for  $V_{GDS}$ . Doing that, we believe we are keeping Gibbs spirit when he writes “We are therefore at liberty to choose such a position for the dividing surface as may for any purpose be convenient” [27]. Since there are as many values of  $n^\sigma$  as possible values of  $V_{GDS}$ , the surface excess amount  $n^\sigma$  should always be provided together with the value of  $V_{GDS}$  chosen by the experimenter. Incidentally, this recommendation is also valid when, after the traditional viewpoint, the GDS is assumed to coincide with the adsorbing surface, especially when microporous: in reality, without the knowledge of the  $V_{GDS}$  chosen for its calculation, any surface excess amount is of limited value. With our proposal, the  $V_{GDS}$  can also be chosen for instance much larger than the volume of the adsorbent (which will result in a much larger  $n^\sigma$ ), or smaller, which will result in a smaller  $n^\sigma$ , even negative in some cases (which can explain the negative values sometimes reported [28,15]) what would not affect the accuracy of the data reporting. The  $V_{GDS}$  can even be chosen equal to zero, as proposed by Gumma and Talu [29], the corresponding  $n^\sigma$  then being called the “net adsorption”.

The part of the “Gibbs exclusion volume” in the calculation of the surface excess amount  $n^\sigma$  has not attracted the attention until now, since it is traditionally assumed, in gas adsorption, that the GDS exactly coincides with the actual probe-accessible surface. This is in line with Gibbs proposal—for the case of plane or moderately curved surfaces—to locate the imaginary GDS “in or very near to the surface of discontinuity” (although we should recognize that this is a condition much difficult to fulfill in the presence of a real microporous adsorbent for which the volume inaccessible to the

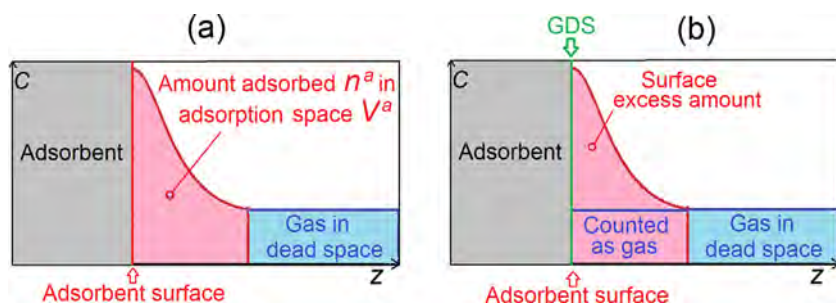


Fig. 4. Simplified representation of the Gibbs model giving adsorptive concentration  $c$  vs. distance  $z$  from adsorbent surface: (a) The real system—(b) representation of the surface excess amount in case the GDS is assumed to coincide with the adsorptive-accessible surface of the adsorbent.



adsorptive is uneasy to determine accurately). Hence a simplified representation of the Gibbs model (e.g. [30,31]), where the adsorptive concentration  $c$  is plotted vs. the distance  $z$  from the surface (cf Fig. 4) and which only takes into account the Gibbs assumption that the volume of the adsorption space (i.e. the adsorbate volume or, still, the thickness of the adsorbed layer) is taken equal to zero. This representation is satisfactory for vapor adsorption below 1 bar: for instance, with help of Eq. (4), one can check that the difference between  $V_{\text{GDS}}$  and  $V_i^s$  can be as high as  $V_i^s$  itself (assuming a standard specific volume  $v_i^s$  of  $0.5 \text{ cm}^3 \text{ g}^{-1}$ ) without introducing in the ( $\text{N}_2$ ) BET area an error higher than  $1 \text{ m}^2 \text{ g}^{-1}$ . This is not any more the case for high-pressure, supercritical, adsorption, where the resulting errors are easily increased by two orders of magnitude. Hence the need to introduce a representation showing the GDS as a precisely defined, geometrical surface, necessarily distinct from any ill-defined physical surface like the surface of a microporous adsorbent. To stress this distinction, Talu [32] calls the GDS a “hyper-surface”.

Fig. 5 introduces this assumption, showing that the geometrically well-defined GDS, symbolized by a straight line, cannot coincide with the more complex shape of the adsorptive-accessible surface of the adsorbent. Fig. 5b tells us that, with this position of the GDS,  $n^\sigma = n^a - n^c$ , where  $n^c$  (corresponding to rectangle C) is the portion of the amount adsorbed which is counted as a gas, after the Gibbs representation, and which makes the difference between  $n^\sigma$  and  $n^a$ .

To each arbitrary position of the GDS (and of the Gibbs exclusion volume) corresponds a different value of the surface excess amount  $n^\sigma$ , as illustrated by Fig. 6. If  $n^b$ ,  $n^c$  and  $n^d$  stand for the amounts of gas represented by rectangles B, C and D, respectively, we can write:

$$n^\sigma = n^a - n^c - n^b \quad \text{for GDS - 1}$$

$$n^\sigma = n^a - n^c \quad \text{for GDS - 2}$$

$$n^\sigma = n^a + n^d \quad \text{for GDS - 3}$$

This freedom in selecting the position of the GDS and the corresponding Gibbs exclusion volume  $V_{\text{GDS}}$  may look somewhat puzzling and uncomfortable for the experimenter. In reality, the practical choice is limited. If we find it indeed more convenient to consider the *specific* Gibbs exclusion volume  $v_{\text{GDS}}$  (per gram of adsorbent, to be easily compared with the specific volume  $v_i^s$  of the adsorbent inaccessible to the adsorptive), then we can conveniently choose between:

- A  $v_{\text{GDS}}$  value close to the adsorbent specific volume  $v_i^s$ , which is essentially justified for vapor adsorption below 1 bar, since, in these experimental conditions, large relative differences

between  $v_{\text{GDS}}$  and  $v_i^s$  still lead to practically similar  $n^\sigma$  and  $n^a$ ; this could also be justified for high-pressure adsorption in case the objective is to assess a surface excess concentration  $\Gamma^\sigma$  and to make a direct use of it, which is rather seldom.

- A  $v_{\text{GDS}}$  value of  $0.5 \text{ cm}^3 \text{ g}^{-1}$  (corresponding to a density of  $2.0 \text{ g cm}^{-3}$ ) which has the advantage (i) of being usually close enough to that of the specific volume  $v_i^s$  of many adsorbents, so that we stay with the excess isotherm shape and height we are accustomed to and (ii) of being, at the same time, a clearly arbitrary value which we have no risk to mix with  $V_i^s$ .
- A  $v_{\text{GDS}}$  value of 0, as suggested by Gumma and Talu [29], which is also of simple application and which, when one is interested by gas storage, immediately shows, if  $n^\sigma$  is positive, the effectiveness of the adsorbent. Let us notice that this value  $V_{\text{GDS}} = 0$  was implicitly used by Dreisbach et al. [33] when providing “the experimental data... without any correction” under the name of “reduced mass of adsorbate”.

For high-pressure, super-critical experiments, choices (b) and (c) are probably more suitable than choice (a) since they are simpler to apply, with no risk of mixing  $v_{\text{GDS}}$  with  $v_i^s$  and they easily lend themselves to an automated procedure carried out by a software.

Of course, the choices above do not allow us to speak of “the” surface excess amount and, even less, of “the right” surface excess amount, since  $n^\sigma$  is simply  $v_{\text{GDS}}$  -dependent.

It may be worth noticing that, in the field of adsorption at the liquid/solid interface, it has been customary, for a long time, to consider positions of the GDS either coincident with the adsorbing surface (e.g. [34]) or not, especially when making use of the concepts of *relative* or *reduced* surface excess amount [35,30].

Let us finally notice that clearly separating the GDS from the probe-accessible surface, like in Fig. 5b, may help reminding that the “precisely determined position” of the GDS (or, better said, the exact value chosen for the Gibbs exclusion volume  $V_{\text{GDS}}$ ) should always be reported together with the surface excess amount  $n^\sigma$  to make it meaningful. Conversely, referring to Fig. 4b where the GDS is superimposed with the probe-accessible surface may let think that the GDS location (and therefore the Gibbs exclusion volume) is to be determined experimentally (which is not compulsory after our proposal) and is prone to the errors related with the dead volume determination (which is not in the spirit of Gibbs views, where the GDS is a “precisely defined... geometrical surface”). The risk is then to completely lose a major interest of the Gibbs model, i.e. the preservation of the basic experimental accuracy.

#### 4. Assessing the amount adsorbed

As reminded in the introduction, the quantity needed both for practical applications of adsorption (determination of surface area, of pore-size distribution...) and for its understanding and inter-

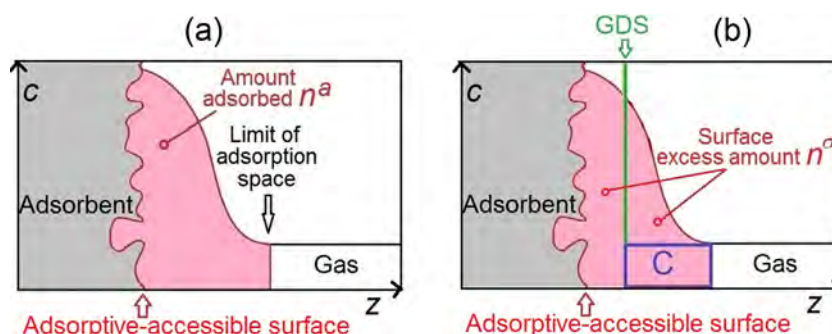


Fig. 5. General representation of the Gibbs model for adsorption on microporous adsorbents. (a) The real system—(b) The Gibbs representation with a GDS distinct from the adsorptive-accessible surface.

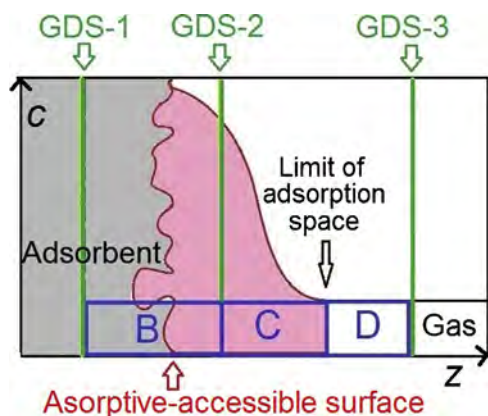


Fig. 6. A few positions of the GDS.

pretation (application of theories, comparison with simulation. . .) is the amount adsorbed  $n^a$ , not the surface excess amount  $n^\sigma$  which is usually assessed, in a first step, from any adsorption manometry or gravimetry experiment. Passing from  $n^\sigma$  to  $n^a$  requires knowing the following data:

- The Gibbs exclusion volume  $V_{\text{GDS}}$  used to calculate  $n^\sigma$ . Most often, this volume is chosen by the experimenter either from his experimental assessment of the dead volume by gas expansion or from the density of the adsorbent (either skeletal density or density of the non-porous material). It should be stressed that the uncertainties about the dead volume or the adsorbent density have no effect on the accuracy of  $n^\sigma$  provided the value used for  $V_{\text{GDS}}$  is known and stated.
- The gas law (ideal or real) also used in the calculation of  $n^\sigma$  to derive the concentration in the gas phase  $c^g$  from the pressure  $p$ .
- The adsorbent volume  $V_i^s$  which is considered inaccessible to the adsorptive «i» used.
- The actual volume  $V_i^a$  of the adsorbate at any stage of the adsorption, i.e. the volume of the adsorption space.

From the above data we can then derive  $n^a$  from  $n^\sigma$  after :

$$n^a = n^\sigma + c^g V_i^a + c^g (V_i^s - V_{\text{GDS}}) \quad (4)$$

(a)                      (b)

where term (a) corresponds to the assumption of zero adsorption volume in the Gibbs model and term (b) takes into account the fact that the GDS does not coincide with the probe-accessible surface of the adsorbent. When these two surfaces are assumed to coincide, like in the simplified representation of Fig. 6, Eq. (4) simplifies into the common form:

$$n^a = n^\sigma + c^g V_i^a \quad (5)$$

In the case of *sub-critical adsorption below 1 bar*, term (a) in Eq. (4) is usually considered small enough to be ignored in comparison with  $n^\sigma$  [8]. If we consider for instance the case of  $\text{N}_2$  adsorption at 77 K with a  $\text{N}_2$  adsorbate density of  $0.8 \text{ g cm}^{-3}$  (assumed to be comparable to the density of the liquid) and a gas density of  $5 \text{ mg cm}^{-3}$  (at 77 K under 1 bar), we see that term (a) accounts for 0.6% of  $n^\sigma$  when the gas pressure is 1 bar, and only for 0.06% when the relative pressure is 0.1, i.e. in the mid of the usual BET range.

Whereas term (b), it can also be usually ignored, essentially, here again, because of the low value of  $c^g$  as compared with the concentration of the adsorbate and provided the difference between the Gibbs exclusion volume  $V_{\text{GDS}}$  and the actual adsorbent volume  $V_i^s$  inaccessible to adsorptive “i” is of the same order of magnitude as the volume  $V_i^a$  of the adsorption space: this is what the experi-

menter usually tries to do by choosing for  $V_{\text{GDS}}$  the apparent  $V_i^s$  as determined by helium expansion.

In the case of super-critical adsorption above 10 bar, the situation is quite different, essentially because of the much smaller difference between the concentrations in the gas and the adsorbed phase. Small errors on the estimation of the volumes of the adsorbent  $V_i^s$  and the adsorption space  $V_i^a$  now have an appreciable influence on the calculated value of the amount adsorbed  $n^a$ .

Let us see for instance the effect of an *uncertainty on the specific volume  $v_i^a$  of the adsorption space*. Even when  $v_i^a$  is assumed to be equal to the specific microporous volume, as commonly done [2,28,36,37,38], an uncertainty of the order of  $0.05 \text{ cm}^3 \text{ g}^{-1}$  (or larger) can easily result from an error in the microporous volume itself, either because the latter was determined with a molecular probe (e.g.  $\text{N}_2$ ) different from the adsorptive or because, due to the solid potential field, the actual density of the adsorbed probe is not homogeneous and differs from the usually assumed density of the liquid: as well stressed by Talu [32], the pore volume then assessed is not strictly speaking a property of the pure solid but a property of the solid/probe gas system. Moreover, in case supercritical adsorption is considered to take place after a mechanism of monolayer surface coverage [3], part of the volume of the wide micropores (i.e. 0.7 to 2 nm wide [5]) does not contribute to  $v_i^a$  once they are able to accommodate more than two adsorbate molecules in width. The situation is still different in the critical temperature region, where a multilayer was shown to take place under high pressure [39,40]. Furthermore, in case the adsorbent is not exclusively microporous (e.g. a number of activated carbons), the actual adsorption space logically also includes a small part of the mesoporous volume. At 100 bar, at room temperature, a  $0.05 \text{ cm}^3 \text{ g}^{-1}$  uncertainty on  $v_i^a$  leads to an uncertainty of 0.2 mmol on the amount adsorbed, i.e. between 4 and 12% of the amount calculated from the surface excess isotherms shown in Fig. 7 and taken as a standard example. Hence the interest of any procedure allowing to improve the accuracy of  $v_i^a$  determination, as recently proposed by Phadungbut et al. [41], although still limited to simulation in the case of a flat adsorbing surface.

Whereas the effect of an *uncertainty about  $v_i^s$ , the specific volume inaccessible to the adsorptive*, it can be indirectly appreciated through the simulation carried out by Do et al. [25] for high-pressure adsorption of argon on graphite at 298 K, simulated in a box whose volume to area ratio is 400 times the collision diameter. Figure 8 gives the areal surface excess amount isotherms, calculated with a Gibbs exclusion volume equal either to the correct adsorbent volume (upper curve) or to an incorrect one, as resulting from erroneous dead volumes with relative errors ranging from only 0.1% to 0.3%. A conversion into adsorbed amount isotherms based on these same correct and incorrect adsorbent volumes would result into an

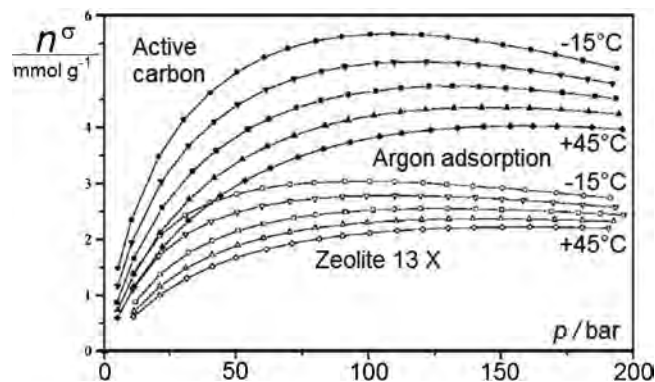


Fig. 7. High-pressure argon surface excess isotherms for a 13 X zeolite (below) and an active carbon (above), from Salem et al. [2].

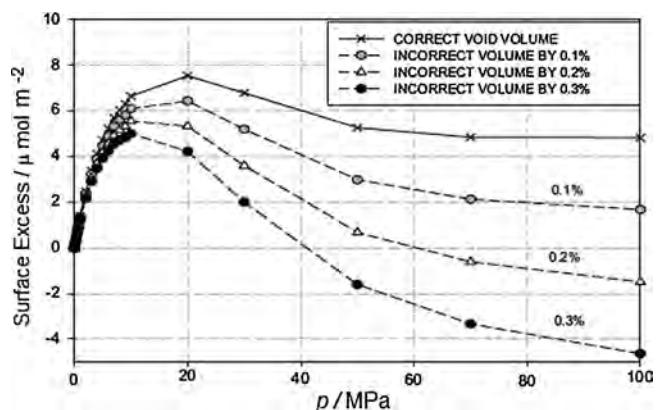


Fig. 8. Effect of dead volume uncertainties on data reported for Ar-graphite system at 298 K, from Do et al. [25].

upward shift and a change in shape, the upper “correct” isotherm then approaching the Langmuir shape and the other isotherms staying beneath, at a distance as large as that seen in Fig. 8.

A more direct examination of the effect of an uncertainty on  $v_{\text{Si}}$  can be made thanks to a recent inter-laboratory comparison of high-pressure methane adsorption on gas shales (Gasparik et al. [42]). We should first stress that this work was carried out very carefully and that it was quite demanding, given the small BET area of the microporous shales examined ( $8 \text{ m}^2 \text{ g}^{-1}$ ). We can therefore consider this work as an interesting reference which, nevertheless, will show us the limits of the current, general, custom of referring to the simplified representation of the Gibbs model shown in Fig. 4b and of dropping, consequently, term  $b$  in Eq. (4). We see indeed in Fig. 9 that the surface excess amounts  $n^{\sigma}$  reported by the seven participating laboratories differ, at 100 bar, from 0.06 to 0.13  $\text{mmol g}^{-1}$ , i.e. from more than simple to double. Nevertheless, because the usual procedure was applied, each surface excess isotherm was calculated with its own GDS, as “automatically” located by a helium dead volume determination.

Fortunately, because this work was carried out and reported with care, it is possible to know, from the data provided, the specific sample volume  $v_{\text{He}}^{\text{S}}$  used as a Gibbs exclusion volume to calculate each surface excess isotherm.

Among the values reported in Fig. 10 we see a relatively small span of only  $0.05 \text{ cm}^3 \text{ g}^{-1}$ , showing again the quality of the work. Unfortunately, in spite of their small value, these variations have a large influence on the value of the surface excess amounts. To

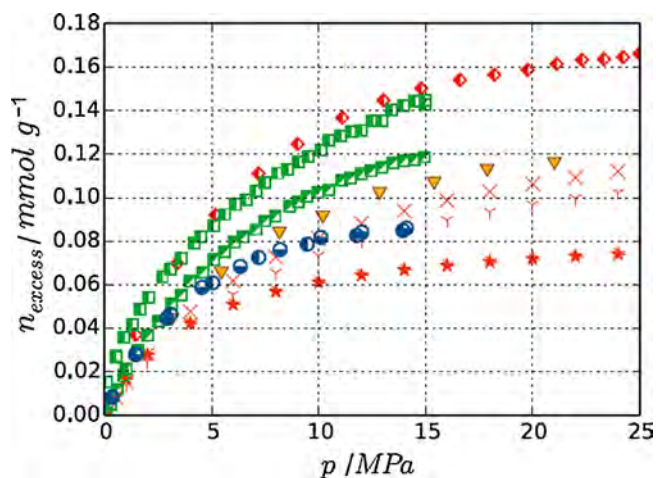


Fig. 9. Surface excess isotherms of methane adsorbed on a Posidonia gas shale at 65 °C (from Gasparik et al. [42]).

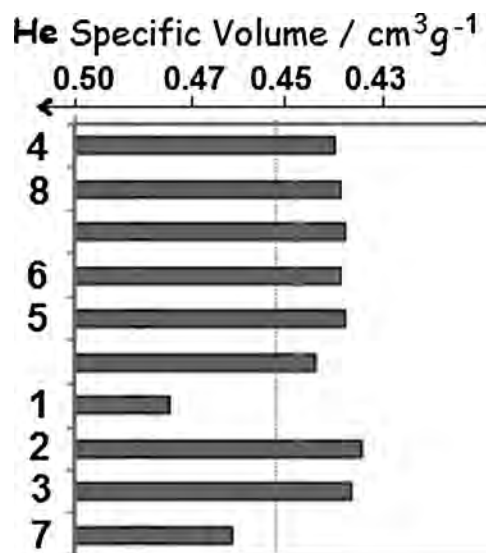


Fig. 10. Specific volumes of Posidonia gas shale determined by He expansion. Same numbering as in Fig. 11. Non-linear scale, because translated from linear density scale (after Gasparik et al. [42]).

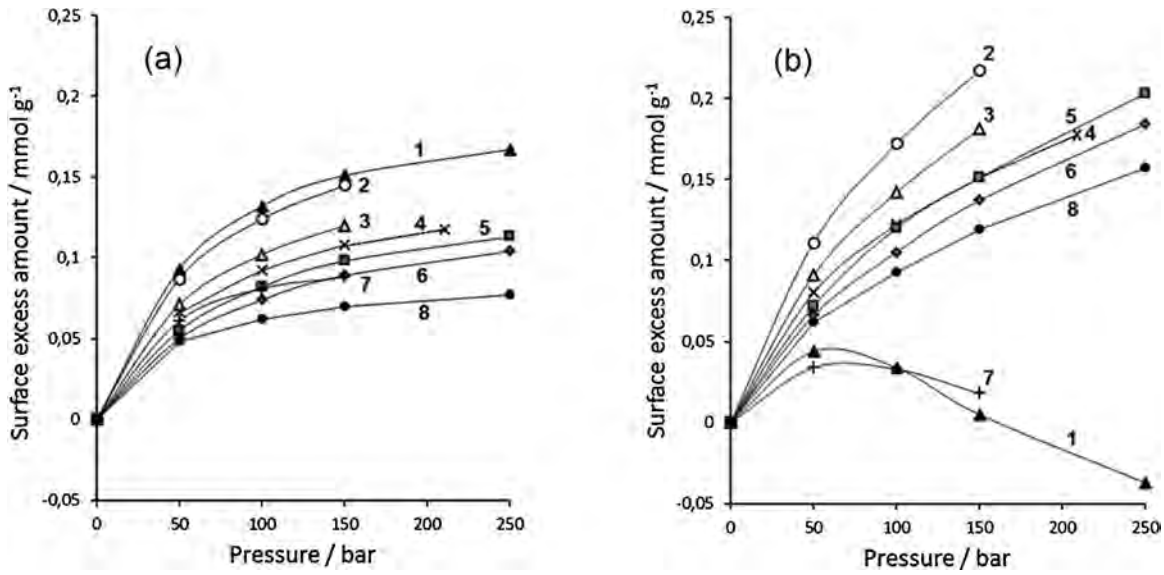
appreciate this influence, we can re-calculate all isotherms of Fig. 9 with a common Gibbs exclusion volume of  $0.45 \text{ cm}^3 \text{ g}^{-1}$ . This allows eliminating from the experimental data all uncertainties related with the dead volume determination. For the calculation, we can make use of Eq. (3) in the form:

$$n^{\sigma} = n - c^{\text{g}}v + c^{\text{g}}v_{\text{GDS}} \quad (6)$$

which shows that a change  $\Delta v_{\text{GDS}}$  in the value chosen for the specific Gibbs exclusion volume results in a change  $c^{\text{g}} \Delta v_{\text{GDS}}$  of the specific surface excess amount  $n^{\sigma}$ . Since we are essentially looking for orders of magnitude we can determine the value of the adsorptive concentration  $c^{\text{g}}$  with help of the ideal gas law (with a real gas law, the concentration would be somewhat higher, and so the change of  $n^{\sigma}$ ).

For the sake of clarity, Fig. 11a simply reproduces the isotherms of Fig. 9, with adequate labeling. As we said, each of these surface excess isotherms was calculated with its own value of the Gibbs exclusion volume which we can estimate, after the data of Fig. 10, to be close to 0.477, 0.437, 0.439, 0.442, 0.440, 0.441, 0.463, and 0.441  $\text{cm}^3 \text{ g}^{-1}$  for isotherms 1–8, respectively. Fig. 11b gives, with the same labeling, the surface excess isotherms calculated with a common specific Gibbs exclusion volume chosen equal to  $0.45 \text{ cm}^3 \text{ g}^{-1}$ . We see that, most unfortunately, eliminating in Fig. 11b the uncertainties in the dead volume determination does not reduce the span but, instead increases it: this simply shows that the part of the other sources of uncertainty is larger than initially thought, especially for isotherms 1 and 7 which are well discriminated from the others by the procedure proposed. These observations lead to the conclusion that (i) although small, the differences resulting from different positions of the GDS (i.e. different values of the Gibbs exclusion volume) are a major source of discrepancy (ii) it is possible to cancel them by simply providing all participating laboratories with the same, conventional but well-defined specific Gibbs exclusion volume  $v_{\text{GDS}}$  which then allows calculating a “dead-volume free” surface excess amount  $n^{\sigma}$  by means of Eqs. (3) or (10) and (iii) it then becomes possible to examine more directly the influence of other sources of discrepancy like sampling, outgassing, calibration of pressure transducers, temperature homogeneity and control etc. . .





**Fig. 11.** Influence of the specific Gibbs exclusion volume  $V_{GDS}$  on the surface excess isotherms of CH<sub>4</sub> on a Posidonia gas shale at 65 °C: (a) Each isotherm calculated with different  $V_{GDS}$ , based on helium dead volume (after Gasparik et al. [42]) (b) All isotherms calculated with same  $V_{GDS}$  of 0.45 cm<sup>3</sup> g<sup>-1</sup>. Symbols correspond to points used to build these curves; experimental points are given in Fig. 9.

## 5. Surface excess and adsorbed amounts in gravimetric experiments

In adsorption gravimetry, the weight increase due to adsorption is alleviated by the buoyancy, proportional to the gas (or fluid) density  $\rho_i^g$ , which, in case of a single-sided magnetic suspension balance, acts over (i) all of its mobile parts in contact with the adsorptive (of volume  $V^B$ , including the sample pan) (ii) the adsorbent proper (of volume  $V^S$ , inaccessible to adsorptive “i”) and (iii) the adsorbed phase (of volume  $V^A$  normally depending on the extent of adsorption) in close interaction with the adsorbent. Reasoning on the masses and calling  $\Delta m$  the measured mass change,  $\Delta \rho_i^g$  the simultaneous density change of the fluid phase and  $\Delta m^a$  the mass adsorbed, we get, for adsorption of a single gas “i” (neglecting, to simplify, the change in  $V^A$ , in line with the assumption that it remains equal to the microporous volume):

$$\Delta m = \Delta m^a - \Delta \rho_i^g (V^B + V^S + V^A)$$

and, introducing the adsorptive molar mass  $M_i$  to pass from  $\Delta m^a$  to the amount adsorbed  $n^a$ :

$$n^a = \frac{\Delta m + \Delta \rho_i^g (V^B + V^S + V^A)}{M_i} \quad (7)$$

where, like in adsorption manometry,  $V^S$  and  $V^A$  are not much easy to estimate with accuracy. To assess the surface excess amount we should make use, by self-consistency, of the same Eq. (4) as that used in adsorption manometry, under the form:

$$n^\sigma = n^a - c_i^g V^A - c_i^g (V^S - V_{GDS}) \quad (8)$$

where all symbols keep the same meaning as in adsorption manometry and where the Gibbs exclusion volume  $V_{GDS}$  is also to be arbitrarily chosen by the experimenter. Being in the scope of gravimetry, we can replace the gas concentration  $c_i^g$  by the ratio  $\rho_i^g/M_i$  where  $\rho_i^g$  is the density of adsorptive “i” in the gas phase and  $M_i$  its molar mass:

$$n^\sigma = n^a - \left( \frac{\Delta \rho_i^g}{M_i} \right) V^A - \left( \frac{\Delta \rho_i^g}{M_i} \right) (V^S - V_{GDS}) \quad (9)$$

By introducing in the latter equation the expression of  $n^a$  given by Eq. (7), we finally get:

$$n^\sigma = \frac{\Delta m + \Delta \rho_i^g (V_{GDS} + V^B)}{M_i} \quad (10)$$

This expression of the surface excess amount has the same basic meaning as expression (3) proposed for adsorption manometry, i.e. (i) it is independent from any assumption about  $V^S$  and  $V^A$ , therefore, keeping the full accuracy of the experiment, and (ii) to be meaningful, the resulting surface excess amount  $n^\sigma$  should be reported together with the value of  $V_{GDS}$  used in its calculation.

We can then draw the amount adsorbed from Eq. (9) which becomes:

$$n^a = n^\sigma + \left( \frac{\Delta \rho_i^g}{M_i} \right) V^A + \left( \frac{\Delta \rho_i^g}{M_i} \right) (V^S - V_{GDS}) \quad (11)$$

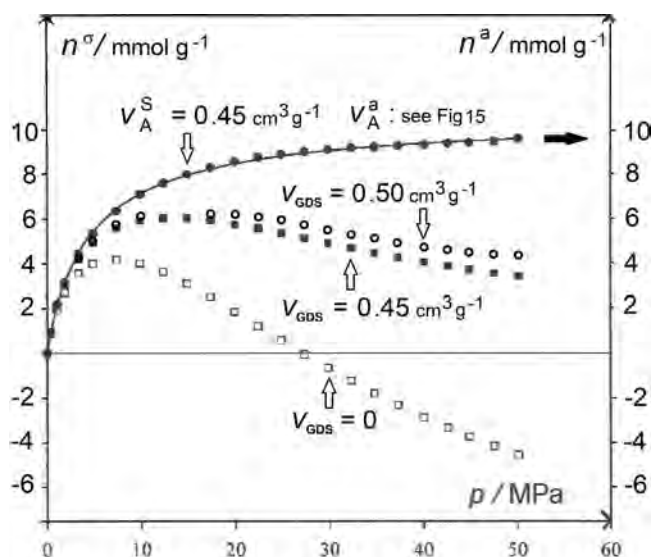
with, here again, like in adsorption manometry (see Eq. (4)) a term taking into account the volume  $V^A$  of the adsorption space and another one, usually skipped, taking into account the difference between the actual volume  $V^S$  of the adsorbent inaccessible to the adsorptive and the Gibbs exclusion volume  $V_{GDS}$  used in the calculation of  $n^\sigma$ . Incidentally, let us notice that, like in adsorption manometry, these two terms (due here to buoyancy) become negligible for adsorption of vapors below 1 bar, so that, here again,  $n^a$  and  $n^\sigma$  can then be considered to be practically identical [43].

It could have been possible to directly calculate the amount adsorbed by inserting our assumed values for  $V^A$  and  $V^S$  in Eq. (7): by skipping the intermediate step of the surface excess amount calculation we would then have lost the possibility of an accurate and assumption-less reporting of the experimental data.

The results of Dreisbach et al. [33], obtained by adsorption gravimetry of argon on active carbon up to 500 bar, allow illustrating the intermediate and relative role of the surface excess amount. This is visible in Fig. 12, in which 3 of the 4 curves are from the original work, although presented here with different ordinates and additional information about the Gibbs exclusion volumes.

The three lower curves are surface excess isotherms which can be assessed by means of Eq. (10) and which were calculated with different values of the specific Gibbs exclusion volume  $V_{GDS}$ , namely 0 (which corresponds to the “reduced mass of adsorbate”), 0.45

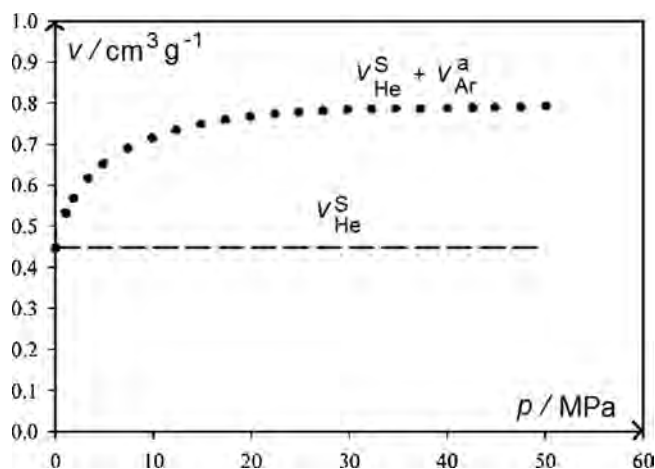




**Fig. 12.** Adsorption of argon on active carbon Norit R1 at 298.15 K (after Dreisbach et al. [33]). Three lower curves: surface excess isotherms with different values of the specific Gibbs exclusion volume  $v_{\text{GDS}}$ . Upper curve: isotherm of amount adsorbed, with corresponding assumptions on solid volume and adsorbate volume.

(where  $v_{\text{GDS}}$  is taken equal to the specific volume of the solid as determined from a helium dead volume) and  $0.50 \text{ cm}^3 \text{ g}^{-1}$  (a value easy to take for the sake of standardization and comparisons; this is the curve we have added to the original ones). We should stress that these three curves, including the lowest one which reports largely negative surface excess amounts above 30 MPa, exactly contain the same amount and quality of experimental information, i.e. the three of them allow calculating exactly the same isotherm of amount adsorbed (the upper curve), with help of Eq. (11), once the adsorptive density vs pressure is known and once the values for the specific adsorbent volume  $v_A^s$  inaccessible to argon and for the specific adsorbate volume  $v_A^a$  are fixed, which is done here with help of the data provided by Fig. 13. Here, the adsorbate volume is assumed to increase with pressure, i.e. not to be constantly equal to the microporous volume.

Incidentally, given the assumptions about the adsorbent and adsorbate volumes which are required to calculate the amount adsorbed and which lead to some final uncertainty, one may prefer, now that the “amount adsorbed” is well defined [2], avoiding



**Fig. 13.** Values taken for the specific solid volume and the specific (solid + adsorbate) volume to calculate the isotherm of amount adsorbed in Fig. 12 (from Dreisbach et al. [33]).

the term “absolute amount adsorbed”, not to give the misleading feeling that this quantity has a kind of absolute value.

#### 4. Conclusions

Our main proposal is to draw full benefit from the Gibbs initial model by considering the calculation of the surface excess amount as a first, intermediate step whose interest is to allow reporting experimental data with keeping the full accuracy of the experiment. For that purpose, it should not include any estimation or uncertain determination of the adsorbent volume inaccessible to the adsorptive. This is made possible once the GDS is given an exact definition, independent from the surface of the adsorbent. An independent GDS also means an independent volume enclosed by the GDS, different from the less well characterized adsorbent volume inaccessible to the adsorptive. Given the central part plaid in the calculation of the surface excess amount by the volume enclosed by the GDS, it may deserve being given a special name and symbol, e.g. the “Gibbs exclusion volume” with symbol  $V_{\text{GDS}}$ . Determining, in a first step, the surface excess amount, does not require any knowledge about the adsorbent or the adsorption mechanism so that this can be done automatically, by a simple software containing a fixed value for the specific Gibbs exclusion volume (e.g. 0.5 or even  $0 \text{ cm}^3 \text{ g}^{-1}$ ). The assumption-free surface excess isotherms then obtained (by either adsorption manometry or adsorption gravimetry) totally lend themselves, even long after being produced, to any new assumption considered necessary to carry out the calculation of the amount adsorbed, provided the Gibbs exclusion volume used in their calculation is stated. It remains possible, at the expense of more work, to use a Gibbs exclusion volume determined by helium expansion, as has been done traditionally until now, but, again, this volume should be stated and reported together with the excess isotherm, to make the latter really meaningful and convertible into an adsorbed amount isotherm, especially when it is found necessary to use a different adsorbent volume.

The assessment of the amount adsorbed is indeed the second, compulsory step of the calculation, since it is required for any application, understanding and simulation of adsorption. This is the step requiring from the experimenter expertise and extra data in order to make a reasonable evaluation of the adsorbent volume inaccessible to the adsorptive (a data difficult to assess when the adsorbent is microporous) and of the volume occupied by the adsorbed phase. This also means that when surface excess isotherms are published alone, they should be provided with any information available about the adsorbent volume  $V_i^s$  inaccessible to the adsorptive and about the microporous volume, if one wants to make it possible to calculate the amounts adsorbed.

A clear separation of the two steps above should be quite rewarding: the automatic and assumption-free assessment of the surface excess amount (with the broad, though precise meaning given in this paper) preserves the accuracy of the experimental data whereas the assessment of the amount adsorbed lends itself to the critical and explicit reasoning of the researcher. This should make it easier to carry out inter-laboratory comparisons of experimental results (by only referring to surface excess amounts) and should help making clear the assumptions used in the derivation of the amount adsorbed, then providing a safe start to the final interpretation.

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