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

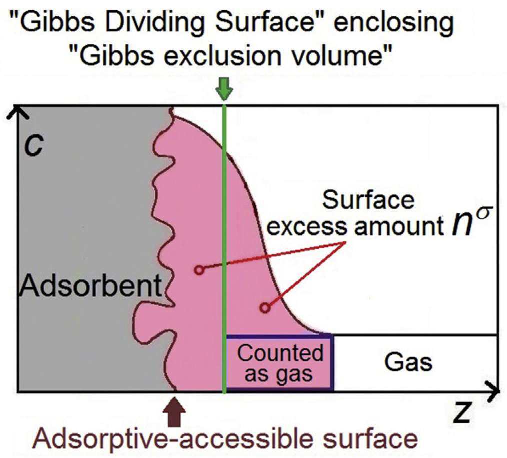
Jean Rouquerol*, Françoise Rouquerol, Phillip Llewellyn, Renaud Denoyel

Aix Marseille Université, CNRS, MADIREL (UMR 7246), 13397 Marseille, France

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.

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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* Corresponding author. Fax: +33 491 882511.
E-mail address: jean.rouquerol@univ-amu.fr (J. Rouquerol).

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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^{σ}	surface excess amount, always relative to a given value of the "Gibbs exclusion volume" V_{GDS} (n^{σ} also stands for the specific surface amount, i.e. per unit mass of adsorbent, depending on the context)
Δm	recorded mass change in adsorption gravimetry experiment
Δm^{a}	mass adsorbed in adsorption gravimetry experiment
$\rho^{g}{}_{i}$	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 (υ if specific, i.e. per unit mass of adsorbent)
$V^{a}{}_{i}$	volume of the adsorption space for adsorptive "i" ($\upsilon^{a}{}_{i}$ if specific, i.e. per unit mass of adsorbent)
$V^{g}{}_{i}$	"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"
$V^{S}{}_{i}$	adsorbent volume inaccessible to adsorptive "i". ($\upsilon^{S}{}_{i}$ if specific, i.e. per unit mass of adsorbent)
$V^{S}{}_{He}$	adsorbent volume inaccessible to helium ($\upsilon^{S}{}_{He}$ if specific, i.e. per unit mass of adsorbent)
V_{GDS}	"Gibbs exclusion volume", i.e. volume enclosed by the GDS (υ_{GDS} if specific, i.e. per unit mass of adsorbent)
$V^{a}{}_{Gibbs}$	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
Γ^{σ}	surface excess concentration n^{σ}/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:

$$n^{a} = n - c^{g}V_{i}^{g} \qquad (1)$$

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 $V^{g}{}_{i}$ (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 $V^{g}{}_{i}$ 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:

$$V_{i}^{g} = V - \left(V_{i}^{S} + V_{i}^{a}\right) \qquad (2)$$

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

2.3. Change of the dead volume as adsorption proceeds

The adsorbate volume $V^{a}{}_{i}$ 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

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