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## A novel method for determining the adsorbed phase volume from an excess adsorption isotherm for an arbitrary adsorbent

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Adsorption volume is an important parameter for characterizing the adsorbent–adsorbate system. In this paper the new method for reliable evaluation of adsorption volume is presented. The validity of the proposed method is tested by 11 experimentally studied systems. The test results indicate that the method has strong potential for practical use.

**Keywords:** adsorption volume, excess adsorption, absolute adsorption.

## Новый метод определения объема адсорбционной фазы по изотерме избыточной адсорбции для адсорбентов произвольной структуры

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Адсорбционный объем является важным параметром для характеристики системы адсорбент – адсорбат. В работе предложен новый метод надежной оценки адсорбционного объема. Метод опробован на 11 экспериментально изученных адсорбционных системах. Показано, что предложенный метод обладает достаточным потенциалом для практического использования.

**Ключевые слова:** адсорбционный объем, избыточная адсорбция, абсолютная адсорбция.

### Introduction

The rigorous determination of absolute adsorption quantities remains to be challenging. This is reflected in the continuing publications on the subject in recent years (see, for example, [1–11]). Yet, it is the entire population of the adsorbed molecules, and not just the excess ones that determines such important quantities as heat of adsorption, dielectric permeability of adsorbed substances, and spectroscopic characteristics of the molecules in the adsorbed states. The same principles are at play in two-dimensional phase transitions and adsorption hysteresis. Lastly, the absolute adsorption quantities are essential parameters of all theoretical adsorption models based on statistical thermodynamics. This is in contrast with excess adsorption models, for which rigorous thermodynamics can be constructed for any type of excess quantities, e.g., Gibbs excess [12], net adsorption [13], or Hill's model of “adsorption in a vessel as an adsorption system” [14]).

Complications arise when the mechanisms of adsorption processes or the state properties of adsorbed substances are to be investigated with using experimentally available excess adsorption isotherms. For the absolute adsorption to be computed, this approach requires the evaluation of the adsorption volume, which in practical applications is an unknown and undefined quantity. In essence, the problem reduces to identifying the adsorption volume that is at play in a given adsorbent-adsorbate system, as well as finding methods of its calculation. In their paper of 1985 [15], Serpinski *et al.* showed that the mere presence of a force field near the surface of a solid is not sufficient to produce the phenomenon of adsorption. The field must be strong enough to change the concentration of the adsorptive by an amount no smaller than the mean concentration fluctuation of the bulk-phase at a given temperature.

## Results and discussion

Excess adsorption is commonly related to absolute adsorption through the equation

$$\Gamma = a - W_p \quad (1)$$

The following physical meaning is attributed to Eq. (1): only part of the total amount  $a$  of an adsorbate present in volume  $W$  is relevant to the existence of an adsorption field, namely, an amount equal to  $\Gamma$ , while another part,  $W\rho$ , being part of the gaseous phase, would occupy volume  $W$ , even in the absence of an adsorption field. This situation is illustrated in Fig. 1, where the region denoted as  $\Gamma$  corresponds to excess adsorption. However, in the rigorous approach to the problem under consideration, we should begin with the following questions: May we write Eq. (1) in this form at all? and Do all of the terms of Eq. (1) have meaning and really exist?

It is easy to understand that the main problems are relevant to value  $W$ , whereas magnitude  $a$  also loses its meaning without  $W$ . As can be seen from Fig. 1,  $\Gamma$  is a finite quantity and is by definition equal to

$$\Gamma = \int_0^{\infty} [\rho(z) - \rho_{\infty}] dz \quad (2)$$

where integration is performed over a coordinate normal to the surface, while for the magnitude  $a$ , we have

$$a = \int_0^{\infty} \rho(z) dz \rightarrow \infty \quad (3)$$

Integral (3) may be finite provided that the upper integration limit is finite, a circumstance that would impart a meaning to the  $W$  value. In other words, we should use some physical considerations to place a boundary with coordinate  $z^*$  at some finite distance from an adsorption surface. The space to the left of the boundary would represent the adsorption volume and that to the right, the gaseous phase. Whereas the adsorption volume of adsorbents, such as zeolites, may be estimated in good approximation one way or another for adsorbents with arbitrary structures, this problem is nevertheless difficult to solve, even approximately. In the above-cited works have been proposed variety of approximate methods for solving this problem.

From equation (1) follows

$$W = K_H^a - K_H^{\Gamma} \quad (4)$$

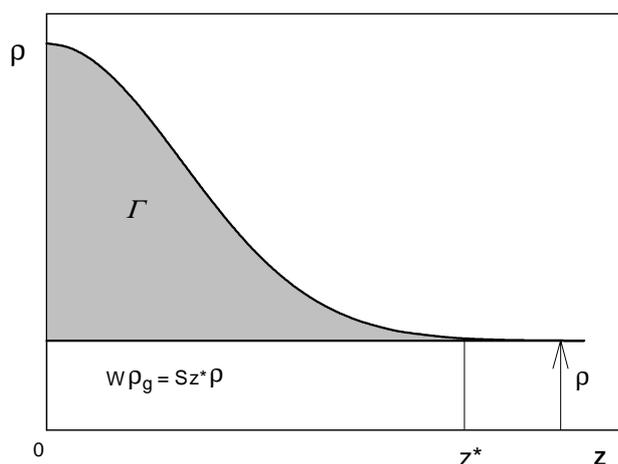


Fig. 1. Schematic representation of the local density of an adsorbate as a function of distance  $z$  from adsorbing surface  $S$ .

Relation (4) is valid even with variable  $W$ , when the adsorption deformation is taken into account.

A rigorous determination of the greatest lower bound for adsorption volume  $W$ . Let us consider a schematic representation of the excess and absolute adsorptions shown in Fig. 2. A straight line  $W\rho$  intersects the curve of excess adsorption  $\Gamma(\rho)$  at some point  $(\rho^*, \Gamma^*)$ , where  $\Gamma^* = W\rho^*$ . According to relation (1), at this point the absolute adsorption equals  $2\Gamma^*$  or  $2W\rho^*$ . On the other hand the maximum absolute adsorption equals  $W\rho_B$ . Taking into account that the absolute adsorption is the ascending and continued function we can write down the following rigorous strict inequality

$$2W\rho^* < W\rho_B \text{ or } \rho^* < \rho_B/2$$

$$\text{By this means } W > \frac{\Gamma(\rho^*)}{\rho^*} = W_{\min}.$$

It is notable that for all systems tested here  $W_{\min}$  falls in the range between  $0.52W$  and  $0.56W$ .

One exception is system with neon, for which  $W_{\min}=0.67W$ . This fact may be used for rough evaluation of the adsorption volume  $W=1.85W_{\min}$ .

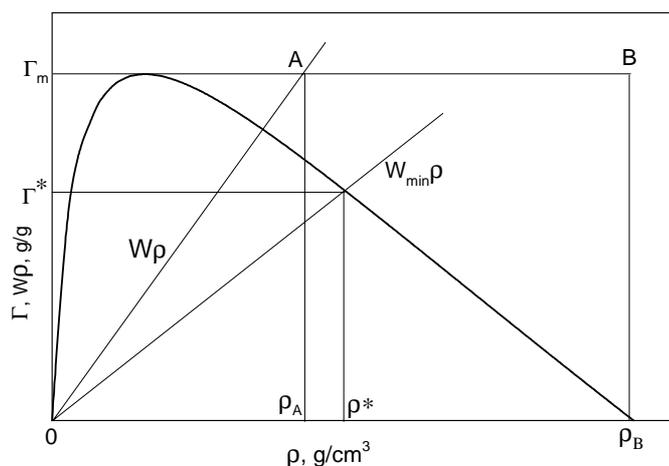


Fig. 2. Schematic representation of the methods of determination  $W$  and  $W_{\min}$ .

Method of determination of adsorption volume. Presented below is a new method of calculation of the adsorption volume from an excess adsorption isotherm on adsorbents

with arbitrary structures. The method demonstrated very strong results for eleven experimentally measured systems. However, its theoretical explanation remains a challenge, which we continue to work on.

Step 1. Determining the area under the curve of the excess adsorption isotherm, i.e. finding the definite integral (see Fig. 2)

$$\int_0^{\rho_B} \Gamma(\rho) d\rho \quad (5)$$

Step 2. Finding the area of the rectangle  $0\Gamma_m B\rho_B$  which is equal to  $\Gamma_m \rho_B$ .

Step 3. Finding the difference between these two areas, i.e. the area above the curve of the excess adsorption isotherm limited by the level  $\Gamma_m = \text{const}$

$$\Gamma_m \rho_B - \int_0^{\rho_B} \Gamma(\rho) d\rho, \quad (6)$$

Step 4. Finding the density  $\rho_A$  on the condition that the rectangle  $0\Gamma_m A\rho_A$  is equal to the difference between two areas found in step 3.

Step 5. Finding the adsorption volume  $W = \tan(\alpha) = \Gamma_m / \rho_A$ .

The steps described above can be represented by a single formula:

$$W = \frac{\Gamma_m^2}{\Gamma_m \rho_B - \int_0^{\rho_B} \Gamma(\rho) d\rho} = \frac{\Gamma_m}{\rho_B - \int_0^{\rho_B} \theta(\rho) d\rho} \quad (7)$$

To test the suggested method we processed eleven experimental excess adsorption isotherms measured on different adsorbents and over a wide range of equilibrium pressures. As the above-described method of estimation of adsorption volume requires to a high degree of accuracy such quantities as the definite integral of the function  $\Gamma$  with respect to the variable  $\rho$  and also the characteristic points  $\Gamma_m$ ,  $\rho_m$  and  $\rho_B$  we used the following empirical equation which provides a very good fit to the experimental excess adsorption data

$$\Gamma = \frac{k_0 \rho}{1 + k_1 \rho + k_2 \rho^2 + \dots + k_n \rho^n} - k_{n+1} \rho \quad (8)$$

As a rule, for all adsorption systems  $n$  was 2 or 3. The calculation results along with a general information about these adsorption systems are summarized in the tables 1 and 2.

Table 1. Adsorption systems used for testing the method

No	Systems
1	Ar – GAC-250, T = 298.15 K [16]
2	CH <sub>4</sub> – GAC-250, T = 298.15 K [16]
3	N <sub>2</sub> – GAC-250, T = 298.15 K [16]
4	Kr – GAC-250, T = 298.15 K [16]
5	Ne – GAC-250, T = 298.15 K [16]
6	CH <sub>4</sub> – BPL, T = 298.15 K [17]
7	CH <sub>4</sub> – Norit R1, T = 298.15 K [18]
8	CH <sub>4</sub> – CMS, T = 313.15 K [19]
9	N <sub>2</sub> – NaA, T = 305.15 K [20]
10	CO <sub>2</sub> – Filtrasorb 400, T = 318.15 K [21]
11	Kr – NaA, T = 373.15 K [22]

Table 2. The initial data and the test results

No of systems	$\Gamma_m$ g/g	$\rho_m$ g/cm <sup>3</sup>	$\rho_B$ g/cm <sup>3</sup>	$\int_0^{\rho_B} \Gamma(\rho) d\rho$ cm <sup>3</sup> /g	W cm <sup>3</sup> /g	$a_0$ g/g
1	0.1875	0.21655	1.2050	0.131179	0.3710	0.4470
2	0.08372	0.058946	0.4028	0.018738	0.4678	0.1884
3	0.11176	0.13876	0.6651	0.041816	0.3841	0.2555
4	0.5004	0.27945	2.1394	0.59888	0.5308	1.1356
5	0.02612	0.32877	0.7438	0.01284	0.1036	0.0771
6	0.08908	0.048607	0.3491	0.018244	0.6172	0.2155
7	0.09783	0.03865	0.2930	0.015123	0.7068	0.2071
8	0.04293	0.04672	0.33499	0.008113	0.2940	0.0985
9	0.06257	0.10001	0.5982	0.021716	0.2491	0.1490
10	0.30870	0.14057	0.89878	0.169274	0.8809	0.7917
11	0.15044	0.30339	1.9152	0.168068	0.1885	0.3610

The method as applied to the real system is illustrated in Fig. 3. The portion of the systems, for which adsorption volume W have been calculated, are shown in Fig. 4 and Fig. 5.

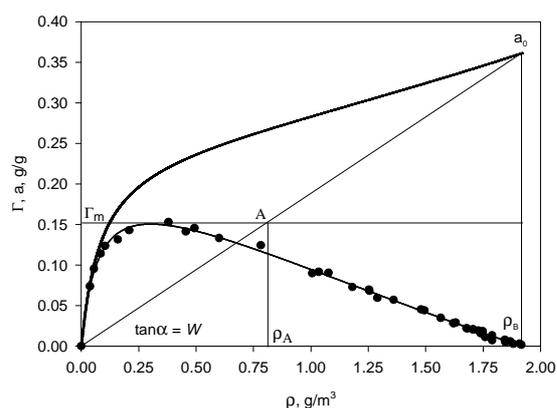


Fig. 3. The experimental isotherm of excess adsorption and calculated absolute adsorption for krypton on zeolite NaA at  $T=373$  K

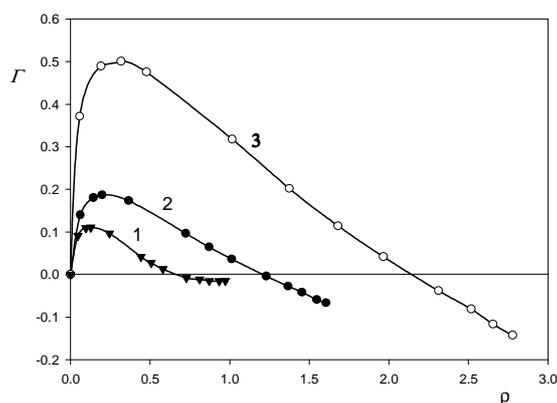


Fig. 4. The isotherms of (1) nitrogen, (2) argon, and (3) krypton excess adsorption on carbon GAC-250 at  $T=298$  K

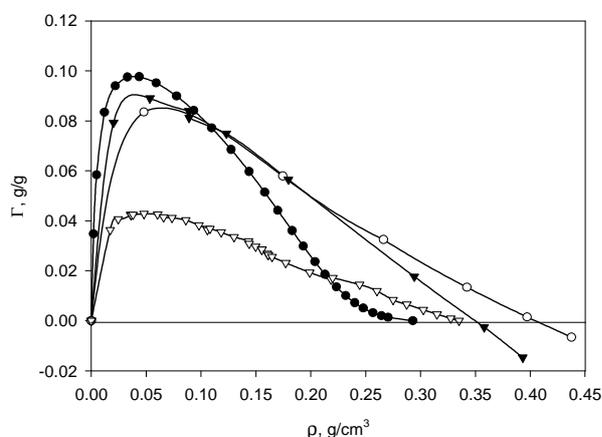


Fig. 5. The excess adsorption isotherms of methane on different adsorbents: ● – Norit R1, 298.15 K; ○ – GAC-250, 298.15 K; ▼ – BPL, 298.15 K; Δ – CMS, 313.15 K.

As we emphasized earlier [5], the adsorption volume is not identical with the crystallographic volume of voids in a solid. It is a volume accessible to adsorbed molecules and dependent on a specific adsorbent – adsorbate pair. It is easy to confirm this through a comparison, for example, of the volumes of the large cavities in zeolite NaX, assessed by the adsorption of six different substances at the same temperature [23]. Scattering amounts to  $\pm 32\%$  of the average pore volume.

## Conclusions

The problem of no contradictory introduction of the notion of the adsorption volume for porous solids of arbitrary structure has been discussed. A new method has been proposed to determine such adsorption volume from the experimental excess adsorption isotherm. In turn the method enables the corresponding absolute adsorption isotherm to be obtained. The method has been tested using eleven experimental adsorption systems consisting of different adsorbents and adsorbates and measured at various temperatures. The experimental data have been taken from literature. All obtained results without exception give quite reasonable values for the adsorption volume. So it is possible to recommend this method for wide use.

In addition, rigorous determination of the greatest lower bound for adsorption volume  $W$  is suggested.

**List of symbols:**  $W$  – Volume of adsorbate in adsorbed phase,  $\text{cm}^3/\text{g}$ ;  $\Gamma$  – Excess adsorption,  $\text{g/g}$ ;  $\Gamma_m$  – Excess adsorption at maximum,  $\text{g/g}$ ;  $a$  – Absolute adsorption,  $\text{g/g}$ ;  $a_0$  – Absolute adsorption at equilibrium gas phase density  $\rho_B$ ,  $\text{g/g}$ ;  $\rho$  – Equilibrium gas phase density,  $\text{g/cm}^3$ ;  $\rho_B$  – Equilibrium gas phase density at  $\Gamma = 0$ ,  $\text{g/cm}^3$ ;  $\theta(\rho) = \Gamma(\rho)/\Gamma_m$  – Relative excess adsorption;  $K_H^a, K_H^\Gamma$  – The Henry coefficients for absolute and excess adsorption isotherms, respectively.

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