Adsorption theory for a mixture of large molecules in slit-like pores with heterogeneous wall surfaces

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The basis of adsorption theory for a mixture of large molecules blocking more than one adsorption site on the surface in the slit-shaped pores with heterogeneous wall surfaces is proposed. The adsorbate-adsorbate lateral interactions are taken into account in the quasi-chemical approximation. A simplified variant of adsorption theory for a binary mixture of molecules of different sizes in two-layer pores with the assumption of complete coverage of the pores is considered. The results of calculations are compared with the experimental data for the benzene – CCl_4 – microporous active carbon adsorbent system. The estimates of the pressure responsible for volume filling of micropores and the effect of nonuniformity of the pore walls on the pressure values are discussed.

1. INTRODUCTION

Real adsorbents are heterogeneous, therefore, the computation of the adsorption characteristics for any concentration of adsorbate must take into account the joint effect of the lateral interactions between the adsorbed molecules and the surface heterogeneity. Large molecules are capable of blocking several neighboring adsorption sites on the adsorbent surface. This complicates dramatically counting possible configurations of adsorbent molecules; therefore, the theory of adsorption of such molecules is much less developed than that for molecules that occupy only one site.

Most adsorption processes occur in porous systems [1]. Depending on the pore width, the joint effect of both pore walls can affect differently the type of adsorbate distribution. This factor is of particular importance for micropores. In this case the conditions for capillary condensation can be dependent on the degree of nonuniformity of the walls. [2,3] In this work the theory of adsorption

of large molecules in pores is considered for the first time. The cluster approach [4] was used to derive the equations describing the adsorption equilibrium. We will restrict our considerations to the case where the adsorbate has the shape of a rectangular parallelepiped $bxdxn$ with the sides b, d, and n. Particular cases of equations for rigid rods of length n and plates of size bxd are easily obtained from the equations for a three-dimensional model of molecules with a hard core. If the pore size becomes so large that the effect of the pore walls on the states of the adsorbate at the pore center can be neglected, we virtually have multilayer adsorption on the open surface of the adsorbent. The theory of adsorption of mixtures of large molecules for this situation has not been developed either yet.

The purpose of the paper is to give a basis of the adsorption theory for mixture of large molecules in the slit-like pores with the heterogeneous wall. A simplified version of the theory for the description of adsorption of a binary mixture consisting of molecules of different sizes located in pores with a diameter equal to two monolayers provided that the pore is completely filled was used to describe the experimental data for the benzene – CCl_4 – microporous adsorbent (active carbon) system [5]. Also the estimates of the pressure responsible for volume filling of micropores; and the effect of nonuniformity of the pore walls on the pressure values are discussed.

2. MODEL

We describe adsorption using a lattice model in which the volume of a slit--like pore is represented as a lattice structure with the number of nearest neighbors equal to z. Let a mixture contains ψ components. The component m, $1 \le m \le \psi$ occupies M_m (M_m is the integer number) sites in the pore volume. Each orientation of adsorbed molecule is characterized by its energetics, which makes it possible to consider it as an individual sort of particles in the case of statistical description of adsorption. Therefore, consideration of different molecular orientations even for a single-component system is reduced to the problem of adsorbing a mixture of molecules of different sizes with a fixed orientation for each of them.

Let us denote the number of possible orientations of the axes of an adsorbed molecule as L_m. This number, characteristic of a given molecule, is determined by the nature of bonds formed between the molecule and the adsorption centers of the adsorbent. For simplicity, we assume that it is a constant for all surface centers (otherwise, the number of possible molecular orientations becomes dependent on the type of adsorption centers). Let us call a "molecule m with orientation λ" by "particle i" ($m, \lambda \leftrightarrow i$), $M_i = M_m$. Let us denote the number of

discernible molecular orientations in the case where the long molecular axis coincides with the one of possible orientations of the axes as s_m. Then $1 \leq i \leq S$, where $S = \sum_{m=1}^{\psi} s_m$. If an external field (in the bulk phase) or an adsorbent field (in the near-surface area) is applied to a molecule, then two situations, where the direction of the long molecular axis coincides with or is opposite to the direction of the orientation axis, should be distinguished for asymmetric molecules; therefore $s_m = 2L_m$. For symmetric molecules, both these cases correspond to the same states and $s_m = L_m$.

Let us consider a lattice structure with $z=6$ and $L=3$ (though, in the general case, molecular orientations can be described in more detail and then $L>z/2$). A scheme of a slit-like pore filled with a rigid linear trimer is shown in Figure 1a: s_m is equal to 3 and 6 for a symmetric and asymmetric trimer, respectively. For a rectangular parallelepiped of dimensions $(b \times d \times n)_m$, the number of "sorts" $s_m=6$, since for each of the three fixed directions of the long molecular axis b_m, two molecular orientations with respect to each of the remaining two axes are possible at $d_m \neq n_m$. Different orientations of the $b_m \times d_m$ face are shown in Figure 1b; the third molecular axis is directed along the third orientation axis. The n value can be arbitrary; however, the cases $n_m=d_m$ or $n_m=b_m$ correspond to spatially degenerated molecular states, so $s_m=3$ as for a rod. For the $(b \times d \times n)_m$ parallelpiped, there are the following dimensions $b_i(a)$ of particle i along the $\alpha(x, y, z)$ axes:

i	1	2	3	4	5	6
x	b_m	b_m	d_m	d_m	n_m	n_m
y	d_m	n_m	b_m	n_m	b_m	d_m
z	n_m	d_m	n_m	b_m	d_m	b_m

Let us take into account lateral interactions between the nearest neighbours. We will characterize intermolecular interactions between the neighbouring particles i and j occupying the sites f and g, respectively, by the energy parameters $\varepsilon^{ij}_{\{f\}\{g\}}$. Let us assume that positive values of the interaction parameters correspond to attraction. Each site of the lattice structure can be either unoccupied or blocked by the adsorbate. We consider an unoccupied site v as the particle of the sort $s+1$. All contacts of this particle are equivalent, $Q_v = Q_{s+1} = z$, and $m_s+1 = 1$. Particles do not interact with unoccupied sites.

In the quasichemical approximation the closed system of equations can be presented as [4]

$$a^i_{\{f\}} P \theta^{m_i v}_{\{f\}} = \theta^i_{\{f\}} \Lambda^i_{\{f\}}, \quad \Lambda^i_{\{f\}} = \sum_{\alpha(n)} \prod_n \theta^{in}_{\{f\}\{g\}} \exp[-\beta \varepsilon^{in}_{\{f\}\{g\}}] / \theta^i_{\{f\}} \quad (1)$$

$$\theta^{in}_{\{f\}\{g\}} \theta^{m_i v, m_n v}_{\{f\}\{g\}} = \theta^{i, m_n v}_{\{f\}\{g\}} \theta^{m_i v, n}_{\{f\}\{g\}} \exp[-\beta \varepsilon^{in}_{\{f\}\{g\}}], \quad t^{in}_{\{f\}\{g\}} = \theta^{in}_{\{f\}\{g\}} / \theta^i_{\{f\}} \quad (2)$$

where $a^i_{\{f\}}$ is the local Henry constant, here P_i is the partial pressure of the i - component, $(i \neq v)$; the index f denotes the site from which we begin counting of blocking sites; $1 \leq f \leq N$; $\theta_{\{f\}}{}^i$ is the probability of filling the local fragment $\{f\}$ by the particle i; $\theta^{m_i v}_{\{f\}}$ is the probability that the local fragment $\{f\}$ of size m_i is free; the symbol $m_i v$ designates the free surface region of the size m_i, in which the adsorption of molecule with orientation i is possible; $\theta_{\{f\}\{g\}}{}^{in}$ is the probability that the particle i on the local fragment $\{f\}$ and the particle n on the local fragment $\{g\}$ are adjacent, here $1 \leq n \leq s$; The normalizing condition to the paired probabilities will be written as $\sum_n \theta^{in}_{\{f\}\{g\}} = \theta^i_{\{f\}}$; the summation over $\alpha(n)$ in Eq.(1) means the sum over all possible arrangements of all adjacent molecules n. The function $\Lambda_{\{f\}}{}^i$ depends on the lateral interactions between the neighbouring molecules.
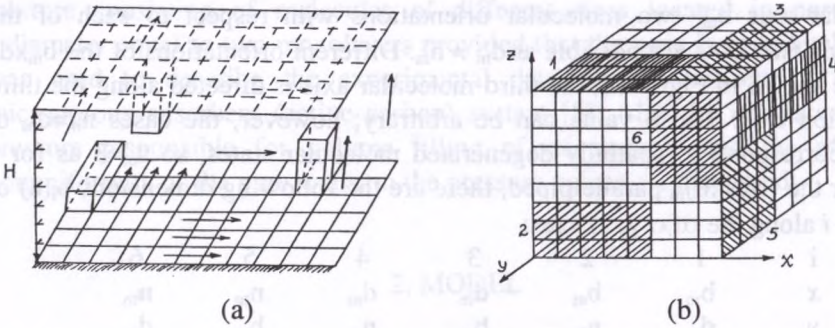

(a)   (b)

Fig. 1. (a) Scheme of a slit-like pore filled with a rigid linear trimer, L=3, z=6. The trimer has three types of orientations: two in the surface plane and one perpendicular to the surface plane. Trimers are schematically shown by arrows, H is the pore width in monolayers. (b) Six types of orientations of the "hard sphere" of a parallelepiped (1-6) that are taken into account when describing the adsorption of large molecules in the slit-like pores at z=6 and L=3. The x and y axes are parallel to the pore walls, the pore width changes along the z axis

The normalizing condition to the probability of coverage of the site with the number f has the form:

$$\rho^v_f + \sum_{i=1}^{L} \sum_{\xi=0}^{m_i-1} \rho^i_{f-\xi} = 1 \tag{3}$$

where $\rho^i_f = \theta_{\{f\}}{}^i / m_i$, the index ξ denotes the shift of the molecule along the given orientation. Normalizing condition (3) reflects the whole totality of different manners of blocking the given site f; ρ^i_f is the probability that the site f is free.

$$\theta_{\{f\}}^{m,v} = \rho_f^v \prod_h t_{hh+1}^{vv},$$ (4)

$$t_{hh+1}^{vv}(k) = \rho_{h+1}^v \left[\rho_{h+1}^v + \sum_i \sum_\varphi \rho_{h+1}^\varphi Q_i^\varphi / z \right]^{-1}$$

where the index h is the number of (m_i-1) sites blocked by the particles i of the size m_i; t_{hh+1}^{vv} is the conventional probability of the free site with the number $(h+1)$ near the free site with the number h; the pair indexes h and $h+1$ specifies the orientation (k) of the pair of free sites; $Q_i^\varphi{}_{(k)}$ is the number of contact of the class φ of the adjacent particle i in the direction specified by the index k.

3. BINARY MIXTURE OF PLANAR MOLECULES IN THE TWO-LAYER PORES

Using general equations (1)-(4), one can construct simpler equations reflecting particular properties of the adsorbents studied. As a simple example, we consider the model situation when the plate-type molecule i (i=A, B) is adsorbed from a binary solution by a microporous adsorbent with a pore size of about two monolayers. The difference between sizes of molecules M_i is related to the difference between their areas. In this case, no effects of molecule reorientation are involved.

It was assumed in the calculations that size S_i of the molecule i equals $S_i = L_i^2$, where L_i is the linear size of the molecule i; and $\varepsilon_{AB} = (\varepsilon_{AA}\varepsilon_{BB})^{1/2}$. The model described here was used to treat experimental data on adsorption of benzene molecules in the micropores of the AC activated carbon from a C_6H_6-CCl_4 solution at 300^0K [5]. In terms of the theory of volume filling of micropores, this adsorbent has a volume of 0.39 cm^3g^{-1} and a pore width of ~1.2 nm [5]. With the given component dimensions, ~0.86 nm (CCl4) and 0.34-0.73 nm (benzene), the two-layer pore model corresponds qualitatively to experimental data. The excess adsorption values found experimentally were converted to total contents using known equations [5]. Typical isotherms are shown in Figure 2 for three sets of parameters (curves 1-3). The two-layer pore model provides a qualitatively correct description of experimental results in a wide range of concentrations. However, for low degrees of coverage of pores with benzene ($\theta_{benzene} < 0.2$), this model does not provide a qualitative agreement with the experiment. The use of this model results in overestimation of the calculated isotherms for high degrees of pore coverage with benzene ($\theta_{benzene} > 0.5$).
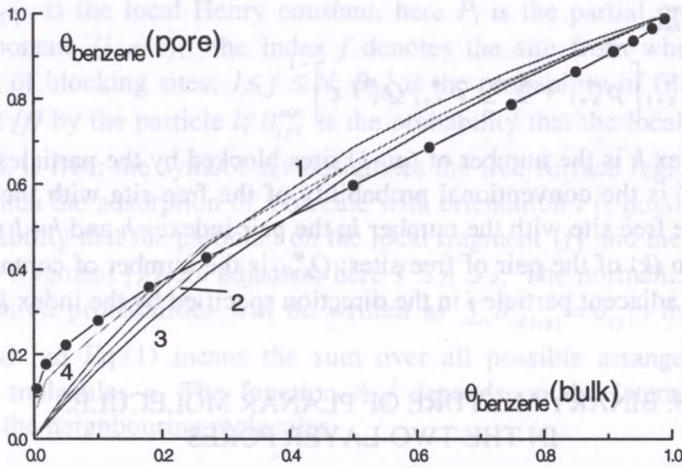
Fig.2. Adsorption of benzene molecules by microporous active carbon AC from a benzene - CCl$_4$ solution at 300K (L$_{benzene}$/L$_{CCl4}$ = 1.07): (1) E$_A$ = 11, E$_B$ = 8.8, ε_{AA} = 1.0, ε_{BB} = 0.76 (2,4); (2) E$_A$ = 17, E$_B$ = 14, ε_{AA} = 1.5, ε_{BB} = 0.76; (3) E$_A$ = 17, E$_B$ = 14.5, ε_{AA} = 1.5, ε_{BB} = 2.0 ; the dots are experimental data [5]. The energy parameters are expressed in the kT unit.

To improve the description of the experiment (see Figure 2, curve 4), it is necessary to reject the condition of homogeneity of the pore walls and to introduce strongly adsorbing sites for molecules A present in a low concentration (~2%) with a binding energy greater than that for the rest of units on the surface by 10kT (for the values of parameters corresponding to curve 2 in Figure 2).

4. MICROPORE VOLUME

For estimation of the micropore volume the Dubinin-Radushkevich equation is actively used [6]. However, the influence of the lateral interaction changes the conditions of pore filling [7-9]. It was shown earlier for simple fluid systems when each molecule occupies one site. Similar estimations are given below for adsorption of large molecules. Figure 3a explains the definitions of the pressures $P_1(H)$ and $P_2(H)$ at which a pore filling occurs. These pressures can be expressed as $P_{1,2}(H) = P_s \exp(-b_{1,2})$, where P_s is the pressure of the saturated vapour, and $b_{1,2}$ is the coefficient depending on the pore width H.

Previously [10], the following analytical estimates of $b_{1,2}(H)$ were obtained for spherically symmetric particles in the absence of specific interactions (inert gases, CH$_4$, N$_2$, O$_2$, and the like molecules): the b_1 value is varied from 1.7 at

H=6 to 4.9 at H=3. Analogously, the b_2+ (the upper estimation) and b_2- (the low estimation) values are changed from 1.2 to 4.9 and from 2.8 to 7.7 respectively at the same H values. Now it has been found that an increase in the size of the molecules leads to an increase in the above coefficients due to the interactions between the molecules and the pore walls and to their decrease (by about 0.4) due to predominant horizontal orientation of the molecules.
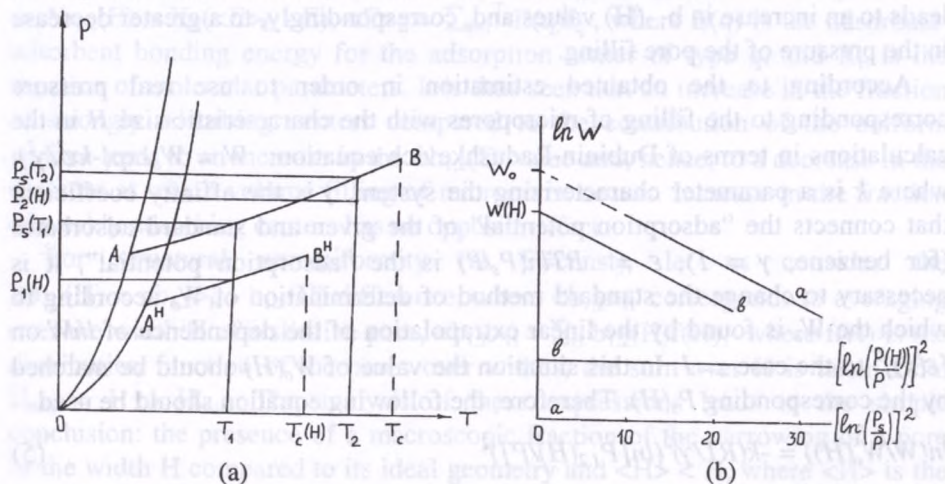
Fig.3. (a) P - T cross-sections of phase diagrams of the adsorption in the bulk phase and the adsorbate in the slit-like pore of width H; T_c and $T_c(H)$ are the critical temperatures; $P_s(T)$ is the saturated vapour pressure at a temperature T; $P_{1,2}(H)$ is the pressure of filling of the micropore volume of width H at T_1 and T_2, respectively.

(b) Adsorption isotherms (1 and 2) in the coordinates of Dubinin-Raduchkevich equation and eq (5) with the corresponding abscissa axes 1 and 2 at pressures lower than the $P(H)$ pressure corresponding to the volume filling of micropores of width H; the dashed section of curve 1 corresponds to the standard procedure of determination of the micropore volume W_o determination

Therefore, the above intervals of the values of the $b_{1,2}(H)$ coefficients are slightly changed for relatively small polyatomic molecules. This conclusion is in good agreement with the experimental data for CCl_4, benzene, cyclohexane (at 25 °C for all systems), and isopentane (at 0 °C) on ammonium phosphomolibdate, [11(25] benzene on hard coal, [12(26] propane on zeolites 5A (at T=273, 323, and 398 K)[13(27], and argon on chabasite (at T from 138 to 195 K). [14(28] Isotherms of these systems become flattened in the θ-P/P_s coordinates in the region from 0.1 to 0.3 P/P_s. These data correspond to b values lying in the range from 2.3 to 1.1. After appropriate correction of the experimental adsorption isotherms for filling of the micropores considered, the above b values should be of the order of 1.3-2.5.

However, the energy contribution will be predominant for large polyatomic molecules and the pressure corresponding to volumes filling of micropores will decrease. The estimates obtained for the plate-shaped molecules provide a correct dependence of the pressure of the volume filling of micropores on the number of layers blocked by a "nonplanar" adsorbate at a fixed pore width, viz., the number of monolayers H decreases as the plate width increases. This leads to an increase in $b_{1,2}(H)$ values and, correspondingly, to a greater decrease in the pressure of the pore filling.

According to the obtained estimation in order to use real pressure corresponding to the filling of micropores with the characteristic size H in the calculations in terms of Dubinin-Radushkevich equation: $W = W_o exp(-k\varepsilon^2/\gamma^2)$, where k is a parameter characterizing the system, γ is the affinity coefficient that connects the "adsorption potential" of the given and standard adsorbates (for benzene, $\gamma = 1$), $\varepsilon = RTln(P_s/P)$ is the "adsorption potential", it is necessary to change the standard method of determination of W_o according to which the W_o is found by the linear extrapolation of the dependence of lnW on $[\varepsilon(x)]^2$ to the case $x=1$. In this situation the value of $W_o(H)$ should be matched by the corresponding $P_s(H)$. Therefore, the following equation should be used

$$ln(W/W_o(H)) = -k(RT/\gamma)^2(ln[P_{1,2}(H)/P])^2 \qquad (5)$$

If the experimental curve is straightened in the coordinates of Eq.(5) (Figure 3b), its intersection with the ordinate axis determines the volume of micropores $W_o(H)$ with the characteristic size H.

5. EFFECT OF NONUNIFORMITY OF THE PORE WALLS

Nonuniformity of the pore walls changes the local distributions of molecules as compared with that for uniform walls. However, it is possible to analyze qualitatively the effect of nonuniformity of the pore walls on the obtained estimates of pressures corresponding to the volume filling of micropores. Two types of nonuniformities, chemical and structural ones, can be distinguished. Chemical nonuniformities modify the energetics of the surface layer without changing the adsorbent structure. Structural nonuniformities have no effect on the chemical composition of the adsorbent; however, they change the structure of the surface layer, thus forming a rough surface at the atomic level. The effects of chemical and structural nonuniformities manifests themselves respectively as changes in the energies of adsorbent-adsorbate bonding E and changes in the local widths H of slit-like pores. Each of these factors changes the local adsorbate distributions and, thus, macroscopic characteristics of the system under study. When analyzing the estimates of pressures corresponding

to volume filling of micropores, it is possible, to the first approximation, to restrict ourselves to consideration of the $b_{1,2}$ coefficients and to compare their values for uniform and nonuniform pore walls.

For chemical nonuniformity of the walls (at H=const), the difference $\Delta b_{1,2}(E) = <b_{1,2}>_E - b_{1,2}$ (where $<b_{1,2}>_E$ corresponds to averaging of the $b_{1,2}$ coefficient over the adsorbate-adsorbent bonding energy E) can be represented as $\Delta b_{1,2}(E) = K_E(<E>_E - E)$, $<E>_E = \sum_{q=1}^T E(q)f_q$, where E(q) is the adsorbate-adsorbent bonding energy for the adsorption center of type q, and K_E is the function of molecular parameters. It is thus seen that an increase in the fraction of strongly adsorbing centers compared to the contribution of the uniform surface leads to an increase in the $\Delta b_{1,2}(E)$ value and, hence, to a decrease in the pressure at which volume filling of micropores occurs. Increase in the fraction of weakly adsorbing centers has an opposite effect.

For structural nonuniformity (at E=const), let us consider the $\Delta b_{1,2}(H) = <b_{1,2}>_H - b_{1,2}(H)$ difference, where $<b_{1,2}>_H$ corresponds to averaging over the width H of a slit-like pore, $<b_{1,2}>_H = \sum_H b_{1,2}(H)f(H)$, where f(H) is the distribution function of the pores over widths, the sum over H is taken from $H_{min} = 1$ to H_{max}. The analysis of these expressions leads to the simple conclusion: the presence of a macroscopic fraction of the narrowing of a pore of the width H compared to its ideal geometry and $<H> < H$, where $<H>$ is the average value, leads to an increase in the $\Delta b_{1,2}(H)$ value and to a decrease in the pressure at which the volume filling of micropores occurs. Increase in the average pore size has an opposite effect.

Under actual conditions, simultaneous existence of both types of nonuniformities of the pore walls is possible. Then, to the first approximation, it can be accepted that the obtained estimates indicate changes in the $b_{1,2}$ values due to the effect of chemical and structural nonuniformities of the pore walls, if averaged values for the bonding energies $<E>$ and the pore widths $<H>$ are used in these expressions.

6. CONCLUSIONS

The theory for adsorption of a mixture of large molecules proposed here, on one hand provides a fairly detailed description of the state of a molecule in the slit-shaped pores with heterogeneous wall surfaces, which is obtained by the numerical Monte Carlo and the molecular dynamics methods, and, on the other hand, makes it possible to design different variants of simplified models with clearly formulated assumptions at the molecular level for the description of experimental data on multicomponent adsorption.

It was shown that filling of micropore volume occurs at a pressure considerably smaller than the vapour saturated pressure, and that the standard procedure of an estimation of micropore volume applying the Dubinin--Radushkevich equation results in overestimated sizes. A way of a more exact finding of mircopore volume by estimation of the pressure of micropore volume filling has been suggested.

REFERENCES

[1] S. J. Gregg and K. G. W. Sing, *Adsorption, Surface Area and Porosity*, London, Academic Press, 1982.

[2] Yu. K. Tovbin and E. V. Votyakov, *Langmuir* 9, 2652 (1993).

[3] E. V. Votyakov, Yu. K. Tovbin, *Russ. J. Phys. Chem.* 68, 287 (1994)

[4] Yu. K. Tovbin, *Theory of Physical Chemistry Processes at a Gas-Solid Interface*, CRC Press: Boca Raton, FL, 1991.

[5] O. G. Larionov, Sc.D. Thesis (Cheristry), Institute of Physical Chemistry USSR Acad. Sci., Moscow, 1975.

[6] M. M. Dubunin, V. L. Radushkevich, *Comm. USSR Acad. Sci.* 55, 331 (1947)

[7] H. Nakanishi, M. E. Fisher, *J. Chem. Phys.* 78, 3279 (1983)

[8] P. Tarasona, U. M. B. Marconi, *R. Evans, Molec. Phys.* 60, 573 (1987)

[9] A.de Kreizer, T. Michalski, G. H. Findenegg, *Pure Appl. Chem.* 63, 1495 (1991)

[10] Yu. K. Tovbin, *Russ. Chem. Bull.* 48, 1450 (1999)

[11] S. J. Gregg, R. Stock, *Trans. Farad. Soc.* 53, 1355 (1957)

[12] D. A. Cadenhead, D. H. Everett, *Conf. on Industrial Carbon and Graphite, Soc. Chem. Industry*, 1958, p.272.

[13] D. M. Ruthven, K. F. Loughlin, *JCS Farad. Trans. 1* 68, 690 (1972)

[14] T. A. Egerton, F. S. Stone, *Trans. Farad. Soc.* 66, 2364 (1970)

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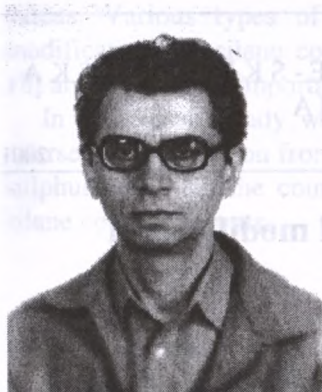
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