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THE POROUS STRUCTURE OF DEHYDRATED INORGANIC GELS

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Analysis of the porous structure of dehydrated inorganic gels which do not swell on sorption usually reduces to the determination of the specific surface of the skeleton from the adsorption branch of the isotherm for a vapour (preferably of nitrogen) at the boiling point and to the calculation of the distribution of the pore volumes with respect to size for the desorption capillary condensation branch of the chosen vapour. Kiselev formulated this analytical system in a most complete form as the "adsorption--structural method"[1,2]. In this method, apart from the specific surface s, calculated from the adsorption branch of the isotherm, the specific surface s' in the general case of a multimolecular adsorption film is determined from the capillary condensation desorption branch for the vapour. If it is assumed that the surface free energy of the adsorption film σ is virtually indistinguishable from the corresponding value for the surface of the bulk liquid phase, thermodynamic considerations show that[1]

$$s' = \frac{1}{\sigma}\int_{a^0}^{a_s} A_a da,$$

where $A_a = RT\ln(p_s/p)$ is the differential molar work of adsorption, a^0 the extent of adsorption at the onset of the irreversible sorption hysteresis during capillary condensation of the vapour, and a_s the limiting extent of sorption at an equilibrium relative pressure $p/p_s = 1$.

In relatively coarsely porous gels, for which the maximum on the pore volume distribution curve with respect to size corresponds to radii $r_m \geq 20$–25 Å, the specific surfaces s' of adsorption films agree quite satisfactorily with the specific surfaces s of the skeletons of the dehydrated gels determined by the BET method[2]. However, for more finely porous gels, for which formal calculation gives $r_m < 15$ Å, $s \gg s'$; this significant discrepancy has not yet received a rational explanation.

In the calculation of the distribution of pore volumes with respect to size on the basis of capillary condensation desorption branches for vapours, based on the application of the Kelvin equation, it is necessary to make an assumption concerning the shape of the pores (usually they are taken to be cylindrical). The pore radii are only effective quantities and the pore volume distribution curve with respect to effective radii corresponds to an equivalent model sorbent with cylindrical pores for which the capillary condensation desorption branch coincides with the desorption branch for the gel under investigation[3,4]. In more accurate calculations corrections are introduced for the thickness of the adsorption films in order to convert the radii of the spaces between adsorption films which are filled during capillary condensation into the effective radii of the gel pores themselves. Various methods of correcting for the thickness of adsorption layers have been analysed by Dubinin and Zhukovskaya[4].

The present paper deals with an examination, on the basis of experimental data, of the possible ways of describing the porous structure of relatively finely porous mineral adsorbents for which $s \gg s'$.

EXPERIMENTAL

The test specimens were commercial silica gels KSK-2.5, KSS-4, KSM-5, KSM-6, alumina gels A-1 and A-2, alumina–silica gels ASK-12 and ASK-24 (the numerals indicate the percentage of Al_2O_3), and a laboratory specimen of finely porous silica gel provided by I. E. Neimark (conventional designation SM). The adsorbents chosen for the investigation were kept for a long time in contact with atmospheric moisture and therefore their surfaces may be regarded as fully hydrated. The

sorption and desorption isotherms for benzene at 20° were investigated for all the specimens by the sorption balance vacuum method in the p/p_s range between 10^{-5}–10^{-4} and 1. Preliminary evacuation of the adsorbents was carried out at 250° to a residual pressure of about 1×10^{-6}. The desorption branches of the isotherms investigated in the region of capillary condensation proved to be typical for relatively uniformly porous gels. Table 1 lists the usual structural characteristics for the adsorbents. V_s denotes the limiting sorption volumes corresponding to $p/p_s = 1$. Particular care was taken to estimate as thoroughly as possible from large scale graphs the relative pressure h_0 corresponding to the onset of irreversible sorption hysteresis. The values of h_0 for all the test adsorbent specimens were in the range 0.15–0.20, the average value of h_0 used to calculate s' being 0.17. The radii r_m are given without correction for the thickness of the adsorption layers. For most of the test adsorbents, except for A-1, KSK-2.5, and A-2, the region of applicability of the BET equation was found to be significantly reduced. Therefore the specific surfaces s of these adsorbents were estimated only approximately. In the calculation of the specific surfaces the molecular area of benzene was taken to be 48 Å², a value typical for adsorbents of the type under consideration.

According to the data of Table 1 for each of the first six adsorbents constituting the first group (r_m = 48–22 Å), the specific surfaces s of the adsorbent skeletons and the specific surfaces s' of the adsorption films are similar, in agreement with the findings of Kiselev[2]. The uniformity of the porous structure of the adsorbents of the first group may be inferred also from the similarity of the average radii $\bar{r}$ calculated from the limiting sorption volumes and the average values of the specific surfaces $\bar{s} = \frac{1}{2}(s + s')$. However, $s \gg s'$ for the adsorbents with $r_m < 15$ Å, belonging to the second group, which is usually explained by the presence of smaller pores, these being filled before the onset of the capillary condensation of the vapour[1].

The BET equation is not very suitable for a quantitative description of the adsorption sections of the isotherm, since under optimum conditions the region of its applicability, expressed in terms of equilibrium relative presures p/p_s, is between 0.02 and 0.35. However, the equation of the adsorption isotherm for adsorbents of the second structural type[5]

$$\log a = M - N \log(p_s/p), \qquad (1)$$

is in good agreement with experimental data in the range of coverages a/a^0 between 0.02–0.05 and 1, where a^0 is the extent of adsorption corresponding to the onset of hysteresis at $h_0 \simeq 0.17$. Figs. 1 and 2 illustrate the applicability of Eqn. (1), which is a variant of the Freundlich equation for adsorbents of the first group. For the KSK-2.5 silica gel, we adopted M = 0.490 and N = 0.552, the extents of adsorption being expressed in millimoles per gramme;

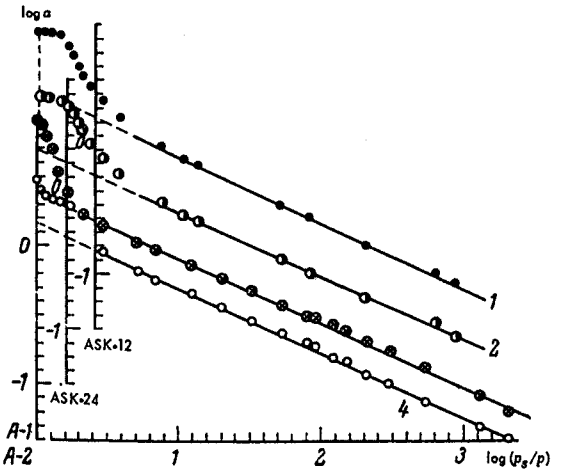


Fig.1. Adsorption isotherms for benzene at 20° plotted in a linear form according to Eqn. (1); adsorbents: 1) ASK-12; 2) ASK-24; 3) A-1; 4) A-2.

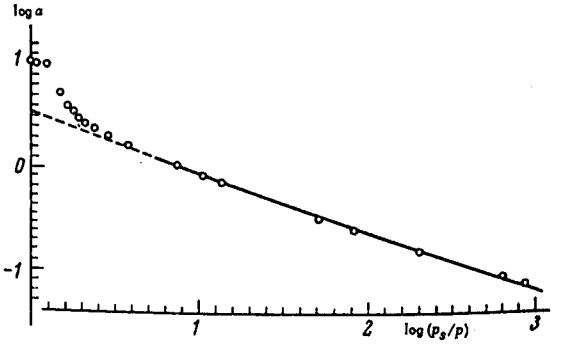


Fig.2. Adsorption isotherms for benzene at 20° in a linear form according to Eqn. (1), on silica gel KSK-2.5.

for the adsorption isotherm adjusted to unit surface area (s = 435 m² g⁻¹), M' = -2.149. The values of M' and N are typical for the adsorption of benzene on the unit surface area of fully hydrated coarsely porous silica gels.

For adsorbents of the first group, the extents of adsorption a^0 corresponding to the onset of irreversible sorption hysteresis are very similar to the extents of adsorption a_m, determined by the BET method, corresponding to the formation of continuous monomolecular layers. Thus for the adsorbents investigated $a_m/a^0 = 1.07 \pm 0.15$, i.e. the discrepancy between a_m and a^0 does not exceed 20%. Consequently before the onset of the capillary condensation of benzene a mainly monomolecular layer forms in the pores of the adsorbents. Earlier this was noted by Dubinin et al.[6] in a study of the secondary porous structure of synthetic type A zeolites. Since deviations of 20% are within the limits of the possible error in the determination of the specific surfaces by the BET method, in the construction of the reduced isotherms it is in this case almost equally permissible to use a_m or a^0. Fig. 3 presents examples of the reduced isotherms for adsorbents of the first group (KSK-2.5 and KSK-4) and the second group (KSM-6); the

TABLE 1. Structural characteristics of the adsorbents.

Adsorbent	V_s, cm³ g⁻¹	r_m, Å	s, m² g⁻¹	s', m² g⁻¹	$\bar{r} = \frac{2V_s}{\bar{s}}$, Å	Adsorbent	V_s, cm³ g⁻¹	r_m, Å	s, m² g⁻¹	s', m² g⁻¹	$\bar{r} = \frac{2V_s}{s}$, Å
A-1	0.596	48	230	280	55	A-2	0.253	22	170	150	31
KSK-2.5	0.888	42	440	460	40	KSM-5	0.427	13	880	200	—
ASK-12	0.492	26	300	320	28	SM	0.393	13	830	170	—
KSS-4	0.694	23	560	510	25	KSM-6	0.226	12	570	25	—
ASK-24	0.423	22	300	320	27						

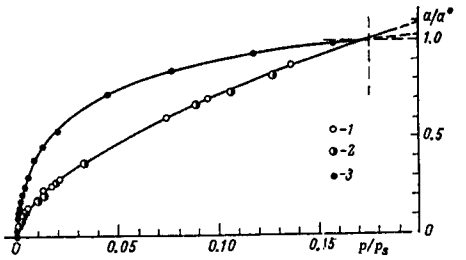


Fig.3. Reduced adsorption isotherms for benzene at 20° on various adsorbents:
1) KSK-2.5; 2) KSS-4; 3) KSM-6.

construction of such curves for adsorbents of this type is a purely formal procedure. The reduced isotherms for adsorbents of the first group coincide satisfactorily. The isotherm for the more finely porous KSM-6 silica gel rises more steeply in the initial adsorption region.

DISCUSSION

The effective radii of the pores of the dominant type, corrected for the thickness of the monomolecular adsorption layers (about 3 Å), in the adsorbents of the first group which have been investigated and which are characterised by similar values of the specific surfaces of the skeleton (s) and the adsorption film (s'), are in the range between 50 and 25 Å. According to the pore dimensions, the adsorbents of the first group are analogous to the transitional pore structures of activated charcoals. For such pores, the curvature of the surfaces does not have an appreciable effect on adsorption, and therefore for adsorbents of the same chemical type the difference in adsorption properties per unit mass is mainly determined by the specific surfaces of the adsorbents. In particular, this is reflected in the virtual coincidence of the reduced adsorption isotherms. For this reason, the parameters of the porous structure of adsorbents of the first group, formed by transitional pores, are the total volume, represented by the limiting sorption volume V_s, the specific surface s ($s < s'$), and the distribution of the pore volumes with respect to the effective radii for the equivalent model sorbent with the given geometrical form of the pores. Since the dimensions of the pores in adsorbents of the first group are much greater than those of the molecules being adsorbed, the adsorption of vapours in these adsorbents may be regarded as occurring on the surface in the adsorption space unbounded by the pore walls. The adsorption-structural method will be used to determine the above parameters of the porous structure of adsorbents of this group [1,2].

The adsorbents of the second group which have been investigated are more finely porous. In the light of the concepts of the corpuscular structure of gels, for example silica gels, the difference between uniformly coarsely porous adsorbents and finely porous adsorbents is mainly associated with a significant increase in the number of points of contact between the spherical non-porous particles or corpuscles, i.e. with the average coordination numbers $\bar{N}$. For example, for a standard series of silica gels, a decrease of the effective radii of pores of the dominant type results in an increase of $\bar{N}$ from 2.4 to 7.4. At the same time there is some decrease in the average diameters of the corpuscles, from 85 to 50 Å.[7]

Studies of the distribution of the number of spherical particles in packed structures based on coordination numbers determined directly in experiments indicate that such distribution is fairly broad. Fig. 4 presents the results of experiments for lead spherical particles[8]. The distribution curve *1* corresponds to lead fragments poured into a cylinder without shaking, the proportion of free interstices between the spherical particles being $\gamma = 0.45$ of the volume of the spherical-particle packed structure, curve *2* corresponds to the fragments poured into the cylinder in small portions and shaken ($\gamma = 0.43$), and curve *3* to the fragments shaken and compacted with a piston ($\gamma = 0.36$). Shaking and in particular compacting of spherical-particle packed structures results in a considerable increase of the proportion of spherical particles in contact with others, i.e. particles with high coordination numbers — up to 12.

A similar situation probably holds for the packing of spherical gel corpuscles which undergo a significant contraction in the drying stage during their preparation. It is easy to show by approximate calculation that in the case of high coordination numbers at the sites of randomly distributed closely packed regions of corpuscles with diameters between 50 and 70 Å, there arise, between the corpuscles in contact, gaps or cavities whose dimensions are typical for micropores. Thus when $N = 12$ the average radii of the cavities are in the range between 6 and 8 Å and when $N = 8$ they are in the range between 10 and 14 Å. Consequently in finely porous silica gels belonging to the second group of the adsorbents under investigation part of the total sorption volume V_s belongs to micropores. The remainder is evidently formed by larger pores which are a variety of transitional pores. These pores constitute gaps between globules at the sites of randomly distributed more loosely packed regions with lower coordination numbers (Fig. 4). Thus finely porous inorganic gels belonging to the second group of adsorbents can be usefully regarded as adsorbents of a mixed type containing micropores and transitional pores.

In the general case the adsorption isotherm for a vapour, for example of benzene, on such mixed type adsorbents is characterised by a distinct hysteresis loop corresponding to the capillary condensation of the vapour in the transitional pores. The specific surface of these pores s_{tr} can be determined from Eqn. (1), since it is approximately equal to the specific surface s' of the adsorption film. Using the known constants M' and N of the adsorption isotherm equation (1) for a uniformly coarsely porous adsorbent of the same chemical type (or simply using a plot of the isotherm

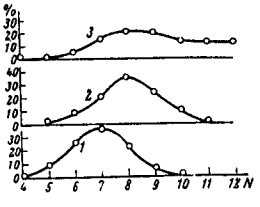


Fig.4. Experimental distribution curves of the number of spheres with respect to the coordination number N for actual types of packing of lead spherical particles.

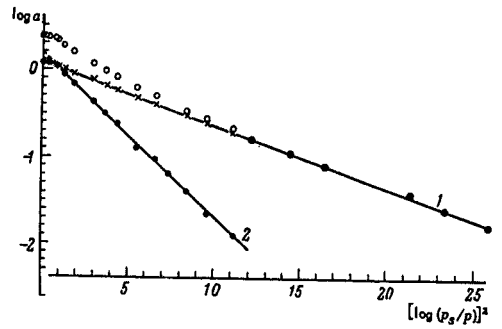


Fig. 5.

TABLE 2. Parameters of the porous structure of silica gels of the second group.

Silica gel	V_s, cm³/g	Variety of pores	s_{tr}, m²/g	W_0, cm³/g	$10^4 B$	V_{mi}, cm³/g	V_{tr}, cm³/g	ΣV_{mi}, cm³/g	$\bar{r}_{tr}$, Å	$\Sigma V_{mi}/V_s$
SM	0.393	transitional	170	—	—	—	0.198	—	23	—
		micro I	—	0.136	2.52	0.120	—	0.195	—	0.50
		micro II	—	0.204	11.7	0.075	—		—	
KSM-5	0.427	transitional	200	—	—	—	0.223	—	22	—
		micro I	—	0.100	1.93	0.091	—	0.204	—	0.48
		micro II	—	0.156	6.61	0.113	—		—	
KSM-6	0.226	transitional	25	—	—	—	0.024	—	19	—
		micro I	—	0.106	1.91	0.097	—	0.202	—	0.89
		micro II	—	0.135	5.03	0.105	—		—	

adjusted to unit surface area), it is easy to calculate the extents of adsorption corresponding to the surface area of the transitional pores and to correct the experimental isotherm for adsorption in such pores. The isotherm corrected in this way will represent the adsorption occurring in the micropores of the given adsorbent. It may be analysed from the standpoint of the theory of the bulk saturation of micropores [9], which describes quantitatively the adsorption of vapours by microporous adsorbents. The method of graphical determination of the parameters of the microporous structure of an adsorbent from the corrected adsorption isotherm has been described in detail by Izotova and Dubinin [10].

Fig. 5 shows the experimental benzene adsorption isotherm on KSM-6 silica gel at 20° plotted in terms of the coordinates of the linear form of the adsorption isotherm equation derived from the theory of the bulk saturation of micropores and corrected for adsorption of the transitional pores. In the range $p/p_s = 3 \times 10^{-4}$–1×10^{-5}, i.e. for $[\log (p_s/p)]^2 > 12$ the experimental points, represented by large filled circles, lie satisfactorily on the straight line *1*, which corresponds to the constants W_{01} and B_1 of the adsorption equation derived from the theory of bulk saturation. However, at higher relative pressures, i.e. for $[\log (p_s/p)]^2 < 12$, the experimental points, represented by open circles, deviate upwards from the straight line. If the differences between the experimental extents of adsorption and the values calculated from the isotherm equation with the constants W_{01} and B_1 for the range $p/p_s = 3 \times 10^{-4}$–0.15 are expressed in terms of the coordinates of the linear form of the equation of the theory of the bulk saturation of micropores, the straight line *2* (Fig. 5) is obtained, which corresponds to the constants W_{02} and B_2. Thus the microporous structure of the KSM-6 silica gel consists of two components. Similar results were obtained also for the finely porous silica gels KSM-5 and SM.

As shown before [9], the limiting volumes of the adsorption space W_0 and the micropore volumes V_{mi}, corresponding to the onset of hysteresis (for benzene at 20° $h_0 = 0.17$), are related by the expression

$$\log \frac{W_0}{V_{mi}} = kB, \qquad (2)$$

from which it is possible to determine the volumes $V_{mi}^{(1)}$ and $V_{mi}^{(2)}$ for the two microporous structures existing in the finely porous silica gels being considered. The difference

$$V_{tr} = V_s - (V_{mi}^{(1)} + V_{mi}^{(2)}), \qquad (3)$$

will represent the volume of the transitional pores of the silica gel with the specific surface $s_{tr} \simeq s'$. Assuming that the pores are of a cylindrical shape, their average effective radius $\bar{r}_{tr}$ is

$$\bar{r}_{tr} = \frac{2V_{tr}}{s_{tr}}. \qquad (4)$$

Table 2 lists the parameters of the porous structure of the finely porous silica gel test specimens.

According to the data in Table 2, the finely porous silica gels investigated have two microporous structures which differ significantly in the values of the parameter B; this shows that the size of the micropores of the dominant type is different in these structures. A similar two-component microporous structure of certain activated charcoals [10] has been confirmed recently by an independent low-angle X-ray diffraction method. Finely porous silica gels are characterised by relatively high average coordination numbers $\bar{N}$ for the packing of corpuscles (about 6 for SM and KSM-5 and about 8 for KSM-6). The various types of the unfilled gaps in the packed corpuscular structures (cavities between the corpuscles in contact, the narrower inlets into such cavities, etc) behave as micropores which may differ significantly in dimensions. Clearly, the probability of the formation in the silica gel structure of larger pores from different types of transitional pores is greater the smaller is the value of $\bar{N}$. The average dimensions $\bar{r}_{tr}$ of the transitional pores existing in the silica gels investigated show a tendency to decrease as $\bar{N}$ increases. The effective radii $\bar{r}_{tr}$ are 23–19 Å when a cylindrical shape is assumed for the pores or 35–28 Å when the cavities are spherical. The proportion of the micropore volume in the total sorption volume V_s increases with $\bar{N}$. The KSM-6 silica gel is virtually a microporous adsorbent.

The adsorption isotherm equation (1) for the so called adsorbents of the second structural type describes the adsorption of vapours on adsorbents with an energetically heterogeneous surface, for which the curvature of the surface does not show an appreciable effect on the extent of adsorption (non-porous or coarsely porous adsorbents). It can be readily demonstrated by formal calculation that sometimes the observed applicability of Eqn. (1) to inorganic finely porous gels is a consequence of the fact that it fits approximately, usually satisfactorily but in a purely mathematical sense, the two-term equation of the adsorption isotherm [Eqn. (7) in Ref. 10] in the case where the parameters B_1 and B_2 for the two microporous structures of the gel differ significantly.

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SUMMARY

1. The porous structures of a number of silica gel, alumina gel, and silica–alumina gel specimens have been analysed on the basis of the adsorption and capillary condensation isotherms for benzene.
2. The pores in relatively coarsely porous gels, for which the specific surfaces of the adsorption films are close to the specific surfaces of the adsorbent skeletons, belong to the class of transitional pores and the parameters of the structure are pore volume, specific surface, and distribution of the pore volumes with respect to dimensions. The arbitrary nature of the distribution curves as characteristics of the porous structure has been noted.
3. The structure of finely porous gels is formed by transitional pores and micropores. A characteristic feature of the finely porous silica gel specimens investigated is the presence of two microporous structures. The proportion of the micropore volume in the total sorption volume increases with the average coordination number for the packing of the corpuscles. The porous structure of such gels is characterised by the parameters of the transitional porosity and constants of the adsorption isotherm equation based on the theory of the bulk saturation of micropores.

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A NEW METHOD FOR THE INVESTIGATION OF THERMAL DIFFUSION IN A MIXTURE OF GASES AND VAPOURS

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In his study of the effect of "foreign" gases on the optical absorption and photoluminescence of the vapours of organic compounds, Neporent[1,2] observed an unusual effect of comparatively small amounts of added gas on the intensity of the absorption and on the luminescence of the test materials. Neporent and his coworkers[1-6] isolated this phenomenon from the accompanying effects and studied it in a number of substances.

Comparison of the characteristics of the phenomenon and the experimental conditions with the theory of diffusion in gases suggests that the observed change in the absorption intensity is due to a change in the concentration of vapour molecules in consequence of thermal diffusion of the test substance and the "foreign" gas in the mixture of vapours[12]. The heterogeneous distribution of temperature in the space containing the mixture, which is necessary for this phenomenon to occur, was a characteristic feature of the experimental technique used by Neporent and coworkers[1-6]. Their results have served as an experimental basis of a method for the investigation of thermal diffusion in a mixture of gases and vapours which is described below. Let us consider a device similar to that used in the study of the optical properties of vapours. The cuvette with the test substance consists of an upper and lower vacuum vessel joined together. An excess of the test substance is placed in the lower vessel in the condensed state to ensure that the vapour in the cuvette is saturated. The temperature maintained in this vessel corresponds to the required vapour pressure.

The upper vessel is fitted with optical windows and is used for the measurement of the absorption or luminescence of the vapour. The temperature of the upper vessel must be higher than that of the lower vessel (otherwise condensation will occur in the upper vessel). In the absence of a "foreign" gas and when the free path is smaller than the dimensions of the cuvette, the concentration of molecules in the upper and lower vessels is given by the usual relation

$$n'_1 T' = n''_1 T'', \qquad (1)$$

where n is the number of molecules per unit volume and T the absolute temperature. Here and subsequently one prime in the symbols for temperature and concentration denotes quantities referring to the upper vessel and two primes denote quantities referring to the lower vessel, the subscript 1 corresponding to vapour molecules and the subscript 2 to the molecules of the "foreign" gas. The additional subscript 1 in n'_{11} denotes the absence of a "foreign" gas. When a "foreign" gas is added, Eqn. (1) breaks down as a result of the effect of the concentration and thermal diffusion processes in the mixture. It is important to note that the vapour concentration in the lower vessel remains the same as before, since it is determined only by the temperature of the condensed phase (the change in the vapour pressure due to a change in the total pressure, smaller than atmospheric, is usually quite insignificant[7]). The