

tinuity on the plot of $\Delta\bar{G}_{O_2}^0(x)$ at 1173°K is apparently due to possible ordering in the $\overline{TiO_2}$ solid solution at $x \approx 1.987$, which involves the formation of dislocations. An analysis of the plots of $\Delta\bar{G}_{O_2}^0(x)$ obtained showed that at temperatures below 1173°K the homogeneity region of TiO_2 is narrow ($\alpha \approx 0.01$ to 0.007), while at higher temperatures it expands considerably to $\alpha \approx 0.027$ (1373°K).

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STANDARDIZED CONTACT POROSIMETRY

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UDC 541.183

The most widely used methods of porosimetry, i.e., the determination of the distribution of the volume of pores according to their radii and their equilibrium capillary pressure, are the methods of mercury porosimetry [1] and capillary condensation [2]. The range of measurable pores in the case of mercury porosimetry is from 20 to 10^6 Å, but it is not applicable in the case of compressible or amalgamating materials. Capillary condensation is used for the porosimetry of very small pores with radii r ranging approximately to 500 to 1000 Å, since the accuracy of the measurement decreases sharply for larger pores [2]. In order to eliminate the shortcomings inherent in the method of mercury porosimetry and to carry out measurements over a broad range of pore radii, we developed the method of standardized contact porosimetry [3]. This method is based on the fact that in a system consisting of a test sample and a porous standard in contact with one another, a capillary-equilibrium distribution of the wetting liquid is established with a variable content of that liquid. The content of the liquid in this system may be varied either through the vapor phase, i.e., by evaporation or condensation, or through the liquid phase, i.e., by capillary evacuating or filling. The capillary equilibrium between the sample and standard in contact means that there is an equality between the capillary pressures P^c for the sample and the standard determined from Laplace's equation

$$P_s^c = P_i^c = -2\sigma \cos \theta / r, \quad (1)$$

where σ is the surface tension of the liquid, θ is the contact wetting angle, and r is the radius of the pore. Equilibrium is achieved owing to a) the percolation of the liquid, b) transfer through the vapor phase (evaporation and condensation), and c) flow of the liquid over the surface film. Owing to the unique relationship between P^c and the relative vapor pressure $\varphi = P/P_0$ (P and P_0 are the vapor pressures over a meniscus and over a flat surface, respectively) defined by Laplace's and Kelvin's equations, in the case of capillary equilibrium there is also an equality between the values of φ . The experiment yields the equilibrium dependence of the volume of the liquid in the pores of the sample under investigation φ_i on its volume in the pores of the standard φ_s , i.e.,

Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow. (Presented by Academician I. V. Petryanov-Sokolov September 24, 1976.) Translated from *Doklady Akademii Nauk SSSR*, Vol. 232, No. 3, pp. 603-606, January, 1977. Original article submitted August 1, 1976.

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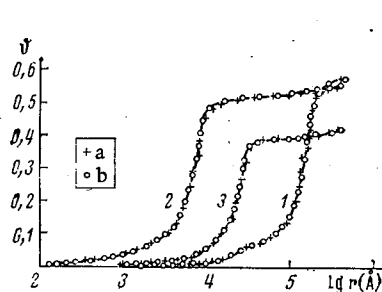


Fig. 1

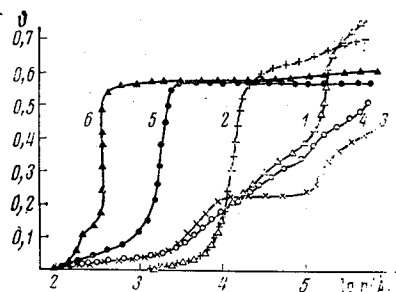


Fig. 2

Fig. 1. Comparison of the porosimetric curves obtained by the methods of contact (a) and mercury (b) porosimetry.

Fig. 2. Integral distribution curves of the pores with respect to their radii for FPIAN-5 (1, 2) and FPP-15 (3, 4) Petryanov filters and platinum black (5, 6).

$$\vartheta_i = f(\vartheta_s) \quad (2)$$

(here and in the following ϑ_i is the relative volume, which is equal to the ratio of the volume of the pores to the total volume of the sample). For the standard it is essential to know the distribution of the pores with respect to the values of P^c or P/P_0 , i.e.,

$$\vartheta_s = \psi_s(P^c); \quad \vartheta_s = \psi_s(P/P_0). \quad (3)$$

From Eqs. (2) and (3) we obtain the sought distribution of the pores in the sample under investigation, i.e.,

$$\vartheta_i = f[\psi_s(P^c)]; \quad \vartheta_i = f[\psi_s(P/P_0)]. \quad (4)$$

If the value of θ is known, we can use Laplace's or Kelvin's equation to go from the expressions in (4) to the distribution of the volume of the pores with respect to their radii r .

In order to experimentally test the method of contact porosimetry, we compared it (the specific conditions included the evaporation of water) to the method of mercury porosimetry. For the comparison we took porous samples which do not amalgamate and do not undergo deformation during mercury porosimetry. Figure 1 shows the porosimetric curves obtained by the contact and mercury methods for metal ceramic samples obtained by the contact and mercury methods for metal ceramic samples of nickel carbonyl (1), of a mixture of nickel carbonyl and Raney nickel (2), and of porous titanium (3). As we see, there is a good fit between the curves obtained. This confirms the hypothesis that the equilibrium distribution of the liquid in a system of porous bodies in contact is determined by the distribution of the pores with respect to the values of P^c or P/P_0 . Under nonequilibrium conditions, for example, during the drying of porous bodies, the gradients of these quantities are the driving forces for the transport of the moisture through the liquid and vapor phases in the pore space [4].

As we have already noted, the application of mercury porosimetry may deform and even destroy the structure [5], resulting in considerable distortions in the porosimetric curves. Taking into account that a liquid with $\sigma = 16$ to 20 dyne/cm can serve as the wetting liquid in contact porosimetry and that the value of σ for mercury is $\sigma_{\text{Hg}} = 480$ dyne/cm, the absolute values of the pressures acting on the skeleton of the porous body are smaller by a factor of 25 to 30 than in the case of mercury porosimetry. An important advantage of the method of contact porosimetry is that during the measurement, the bodies under investigation are in a state similar to the natural working state, which is determined mainly by the pressing force under the conditions of wetting by the liquid in the case of a large class of porous materials (filters, separators, and electrodes). Figure 2 presents the integral distribution curves of the pores with respect to their radii for FPIAN-5 and FPP-15 Petryanov filters, which are widely used in various branches of industry, as measured by the methods of contact porosimetry (evaporation of decane, curves 1 and 3) and mercury porosimetry (2 and 4). As we see, the mercury-porosimetric curves differ significantly from the contact-porosimetric curves. A fit is observed only in the region of the very small pores, which clearly form the strong microstructure of the fibers. Mercury porosimetry is not applicable for many metals which interact with mercury [6]. Figure 2 presents a comparison of the curves obtained by contact (curve 5) and mercury porosimetry (curve 6) for a sample of platinum black. As we see from Fig. 2, mercury porosimetry yields an overestimated volume of the large

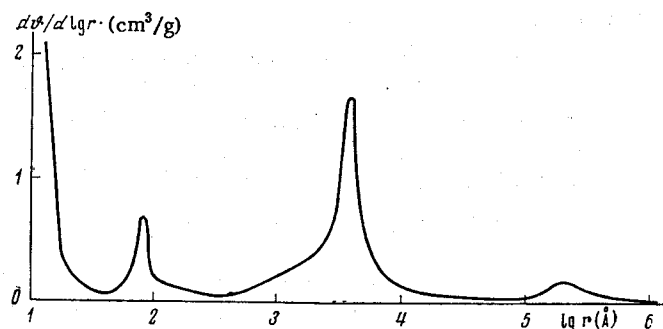


Fig. 3. Differential porosimetric curve for a sample from a mixture of carbon AG-3 and PTFE.

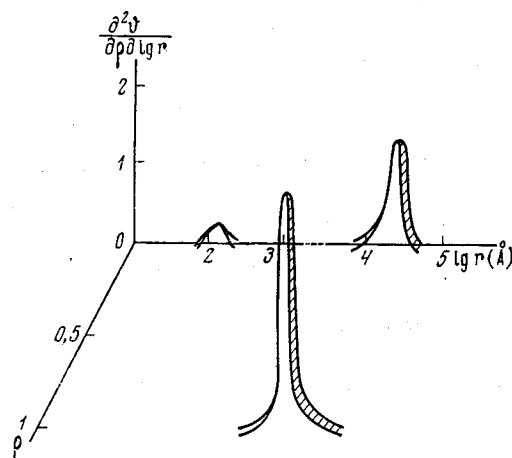


Fig. 4. Differential distribution function of the pores with respect to their radii and with respect to their waterproofness factors ρ .

pores (evidently because of the preferential amalgamation of the pores in contact with the mercury) and an overestimated volume of the pores in the 100 to 1000 Å range (amalgamation of the walls of the pores results in a decrease in their dimensions).

Contact porosimetry permits measurement of the porosimetric curves over a broad range of pore radii from $r = 10$ Å to $r = 10^7$ Å. The lower limit is due to the commensurate relationship between the size of the pores and the size of the liquid molecules and the inapplicability of Kelvin's law in that case, and the upper limit is due to the influence of the gravitational field on the capillary equilibrium. As an example, Fig. 3 presents a differential porosimetric curve for an electrode made from a mixture of carbon AG-3 and PTFE (30 wt.%), which was obtained by contact porosimetry (the working liquid was octane). In order to carry out the measurements over so broad a range of pore sizes, three types of standards were used. Silica Gel KSK-2 was used for values of r ranging from 15 to 200 Å. Its porosimetric curve was obtained by capillary condensation [7]. A sample of a mixture of Raney nickel and nickel carbonyl was used for values of r ranging from 10^2 to 10^4 Å. A sample of nickel carbonyl with a blowing agent was used for values of r ranging from 10^4 to 10^6 Å. These standards were measured by mercury porosimetry. In the case of the very small pores ranging up to 500 Å, the thickness of the adsorption film was taken into account according to the technique adopted for the capillary condensation method in [2].

Standardized contact porosimetry makes it possible to study not only the structure of one-component porous media, but also the structures of multicomponent porous media with different contact wetting angles, which are complex from the point of view of capillary phenomena. An example of a two-component system is a PTFE-waterproofed platinum electrode obtained by mixing the catalyst with a PTFE suspension, subsequent molding, and sintering. In [8] it was shown that an electrode of this type consists of a mixture of two porous masses, viz., a hydrophilic (catalyst particles with $\theta_c = 0^\circ$) and a hydrophobic (agglomerated PTFE particles with $\theta_{\text{PTFE}} > 90^\circ$). The fraction of the mixing of these masses is insignificant. Such a structure clearly calls

for the measurement of the distribution of the pores with respect to the radii and with respect to the water-proofness factors ρ (ρ is the fraction of the surface of the pore covered by PTFE). In order to measure such a curve, the distribution curve of the pores with respect to the radii $\vartheta = \psi(r)$ is first measured by standardized porosimetry with a liquid which completely wets both the catalyst and the PTFE ($\cos \theta_{\text{PTFE}} = \cos \theta_c = 1$). Then the distribution of the hydrophilic pores $\vartheta_{\text{phi}} = \psi_{\text{phi}}(r)$ is measured by standardized contact porosimetry with a liquid (usually water) which wets the catalyst ($\theta_c < 90^\circ$) and does not wet PTFE ($\theta_{\text{PTFE}} > 90^\circ$). The distribution curve of the hydrophobic pores with respect to the radii is obtained by subtraction, i.e., $\vartheta - \vartheta_{\text{phi}} = \vartheta_{\text{pho}} = \psi(r) - \psi_{\text{phi}}(r) = \psi_{\text{pho}}(r)$. Figure 4 presents a differential distribution function of the pores with respect to the radii and with respect to the waterproofness factors obtained by the method just described. Such a curve may, in particular, yield complete information on the capillary equilibrium with the filling of the pores of the electrode by an liquid. Contact porosimetry has also been used to determine the contact wetting angles of PTFE by various liquids [9].

Unlike mercury porosimetry, contact porosimetry offers the possibility of the further use of the samples studied for any other investigations. The principle of porosimetry described in the foregoing, which is distinguished by its experimental simplicity, will make it possible to solve a broad spectrum of problems related to the investigation of the structure of practically any porous medium.

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EVALUATION OF THE POSITION OF THE FERMI LEVEL FROM SOLUBILITY DATA IN BINARY SEMICONDUCTOR-DOPING COMPONENT SYSTEMS

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UDC 541.12.012.2

The main point in the doping of semiconductors is to bring about a directed change in the position of the Fermi level as a result of the introduction of atoms of donor or acceptor doping components into the solution.

The position of the Fermi level can be evaluated on the basis of experimental data on the conductivity, Hall effect, thermoelectromotive force, etc., as indicated by the basic relationships in the physics of semiconductors (see, for example, [1]). In addition, attempts have been made to solve this problem theoretically [2-6].

In the present report we shall propose a method for the evaluation of the position of the Fermi level on the basis of a thermodynamic treatment of the heterogeneous equilibrium between the solid and liquid phases in the approximation of regular solutions with consideration of the extent of ionization of the atoms of the doping components.

The ionization of the atoms of the donors or acceptors plays a great role in the establishment of hetero-

Moscow Institute of Electronic Technology. (Presented by Academician N. M. Zhavoronkov September 6, 1976.) Translated from *Doklady Akademii Nauk SSSR*, Vol. 232, No. 3, pp. 607-610, January, 1977. Original article submitted August 20, 1976.

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