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# PHYSICAL CHEMISTRY

M. A. BUKHBINDER

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## Abstract

## Full Text

PHYSICAL CHEMISTRY

M. A. BUKHBINDER

# ON THE DISTRIBUTION LAW OF THE SPECIFIC SURFACE AREA OF PORES IN AN ISOTROPIC POROUS MEDIUM

*(Presented by Academician A. N. Frumkin, January 20, 1965)*

The specific surface area of pores  $s$  is measured by the ratio of the area  $S$  of the pore surface bounding a certain region of pore space to the volume  $V$  of this region:

$$s = S/V. \quad (1)$$

If the volume  $V$  is chosen sufficiently small, then the quantity  $s$  will change in passing from one region of pore space to another. It is therefore natural to consider the specific surface area of pores as a function of two random variables  $S$  and  $V$ , connected with them by relation (1).

In the present work an attempt is made to find the distribution law of the random variable  $s$ . This problem is solved only for isotropic porous media.

Let us draw in the porous medium a number of lines arbitrarily oriented in space—random secants. The points of intersection of the pore surface with the secants will divide the latter into a number of segments. Those of the segments that fall within the pore space will be called intervals and denoted by  $f$ . Next, let us select in the porous medium cylinders whose axes will be the random secants. These cylinders will cut out on the surface  $S$  areas  $\Delta S$ , each of which (for a sufficiently small area  $\Delta\omega$  of the cylinder cross section) may be regarded as part of a plane. Then, for the  $i$ -th cylinder of length  $f_i$ , the specific surface area of the pores will be equal to

$$s_i = \frac{\Delta S_{i-1} + \Delta S_i}{V_i} = \frac{\Delta\omega \sec \alpha_{i-1} + \Delta\omega \sec \alpha_i}{\Delta\omega f_i} = \frac{\sec \alpha_{i-1} + \sec \alpha_i}{f_i}, \quad (2)$$

where  $\alpha_{i-1}$  and  $\alpha_i$  are the acute angles between the secant and the normals to the areas  $\Delta S_{i-1}$  and  $\Delta S_i$  adjoining the interval  $f_i$ .

In deriving the distribution law of  $s$ , we shall assume that  $\alpha_{i-1}$ ,  $\alpha_i$ , and  $f_i$  are mutually independent.

As is known, the distribution function of  $s$  is

$$G(\sigma) = \mathbf{P}\{s \leq \sigma\} = \int_0^\infty G_2(\sigma\varphi) dG_3(\varphi) = \int_0^\infty G_2(\sigma\varphi) g_3(\varphi) d\varphi \quad (3)$$

and the distribution density of  $s$  is

$$g(\sigma) = G'(\sigma) = \int_0^\infty \varphi g_2(\sigma\varphi) dG_3(\varphi) = \int_0^\infty \varphi g_2(\sigma\varphi) g_3(\varphi) d\varphi, \quad (4)$$

where  $G_2(\sigma\varphi) = G_2(\eta) = \mathbf{P}\{y \leq \eta\}$  is the distribution function of the quantity  $y = \sec \alpha_{i-1} + \sec \alpha_i$ ;  $G_3(\varphi) = \mathbf{P}\{f \leq \varphi\}$  is the distribution function of the quantity  $f$ ; and  $g_2(\sigma\varphi) = g_2(\eta)$  and  $g_3(\varphi)$  are the distribution densities of the quantities  $y$  and  $f$ .

Let us find the distribution law of the quantity  $x = \sec \alpha$ . By virtue of the isotropy of the porous medium, any orientation of the elements  $\Delta S$  in space is equally probable. Therefore, if all the elements  $\Delta S$  contained in some region of the porous medium are translated parallel to themselves onto a spherical surface, then (as  $\Delta S \rightarrow 0$ ) they will be distributed uniformly on this surface. It follows from this that the angle  $\alpha$  has the same distribution as the angle between a random secant and the normal to the surface of the sphere at the point of intersection.

The randomness in drawing secants presupposes their uniform placement in space. Therefore, in deriving the distribution of  $\sec \alpha$ , we shall assume that the points of intersection of the secants with a great circle perpendicular to the direction of the secants are uniformly distributed over the entire area of this circle. Then the distribution function of  $x$  is

$$\begin{aligned} G_1(\xi) &= \mathbf{P}\{x \leq \xi\} = \mathbf{P}\{\sec \alpha \leq \xi\} = \mathbf{P}\{\cos \alpha \geq 1/\xi\} = \\ &= \mathbf{P}\{\sin \alpha \leq \sqrt{1 - 1/\xi^2}\} = 1 - 1/\xi^2 \quad (\xi \geq 1) \end{aligned} \quad (5)$$

and the density of the distribution of  $x$  is

$$g_1(\xi) = G'_1(\xi) = \begin{cases} 0, & \text{for } \xi < 1, \\ 2/\xi^3, & \text{for } \xi \geq 1. \end{cases} \quad (6)$$

We find the distribution of the quantity  $y = \sec \alpha_{i-1} + \sec \alpha_i$ . Since  $\alpha_{i-1}$  and  $\alpha_i$  are independent, the distribution function of  $y$  is equal to the convolution of the distribution functions of  $\sec \alpha_{i-1}$  and  $\sec \alpha_i$ :

$$G_2(\eta) = \mathbf{P}\{y \leq \eta\} = \int_1^{\eta-1} G_1(\eta - \xi) dG_1(\xi) = \int_1^{\eta-1} G_1(\eta - \xi) g_1(\xi) d\xi \quad (7)$$

or

$$G_2(\eta) = \begin{cases} 0, & \text{for } \eta < 2, \\ \int_1^{\eta-1} \frac{2}{\xi^3} \left[ 1 - \frac{1}{(\eta - \xi)^2} \right] d\xi, & \text{for } \eta \geq 2. \end{cases} \quad (8)$$

Integrating, we obtain

$$G_2(\eta) = \begin{cases} 0, & \text{for } \eta < 2, \\ 1 - \frac{1}{(\eta - 1)^2} + \frac{1}{\eta^4} \left[ \frac{1}{2(\eta - 1)^2} + \frac{4}{\eta - 1} + 3 \ln \frac{1}{(\eta - 1)^2} - 4(\eta - 1) - \frac{(\eta - 1)^2}{2} \right], & \text{for } \eta \geq 2. \end{cases} \quad (9)$$

The density of the distribution of  $y$  is

$$g_2(\eta) = G_2'(\eta) = \int_1^{\eta-1} g_1(\eta - \xi) g_1(\xi) d\xi$$

or

$$g_2(\eta) = \begin{cases} 0, & \text{for } \eta < 2, \\ 4 \int_1^{\eta-1} \frac{d\xi}{\xi^3(\eta - \xi)^3}, & \text{for } \eta \geq 2. \end{cases} \quad (10)$$

Integrating, we obtain

$$g_2(\eta) = \begin{cases} 0, & \text{for } \eta < 2, \\ \frac{4}{\eta^5} \left[ (\eta - 1)^2 + 8(\eta - 1) + 6 \ln(\eta - 1)^2 - \frac{8}{\eta - 1} - \frac{1}{(\eta - 1)^2} \right], & \text{for } \eta \geq 2. \end{cases} \quad (11)$$

The graph of the function  $g_2(\eta)$  is shown in Fig. 1.

The distribution function  $G_3(\varphi)$  of the positive quantity  $f$

$$G_3(\varphi) = \begin{cases} P\{f \leq \varphi\}, & \text{for } \varphi > 0, \\ 0, & \text{for } \varphi \leq 0 \end{cases} \quad (12)$$

can be found by direct measurement of a sufficiently large number of intervals  $f$  on a section (polished section) of the porous medium. Since

Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

**Fig. 1**

**Fig. 2**

in this case we obtain the function  $G_3(\varphi)$  in tabular form, formulas (3) and (4) cannot be used directly. Therefore we replace the integrals in these formulas by sums:

$$G(\sigma) \approx p_1 G_2(h\sigma/2) + p_2 G_2(3h\sigma/2) + p_3 G_2(5h\sigma/2) + \dots, \quad (13)$$

$$g(\sigma) \approx (p_1 h/2) g_2(h\sigma/2) + (3p_2 h/2) g_2(3h\sigma/2) + (5h p_3/2) g_2(5h\sigma/2) + \dots \quad (14)$$

Here  $p_1, p_2, p_3, \dots$  are the relative frequencies of  $f$  in the intervals  $(0, h)$ ,  $(h, 2h)$ ,  $(2h, 3h)$ ,  $\dots$

The graph of the function  $g_3(\varphi)$  for sand with mean diameter  $d_{cp} = 0.62$  mm and the graph of the corresponding function  $g(\sigma)$  are shown in Fig. 2.

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*Note: Figure translations are in progress. See original paper for figures.*

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