HYSTERESIS IN SORPTION—X

Open Pore Volume in Relation to Particle Radius

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Introduction

To explain the interesting phenomenon of Drift with other changes of the hysteresis loop in the sorption of water on ferric oxide gel, a theory of the coalescence of the particles of the porous system accompanying successive sorption and desorption has been advanced. In support of the theory a mathematical formulation has been made which relates the cavity volume with particle radius in a system of closely packed spherical particles of equi-radius. The formula indicates that mass remaining the same, the total cavity volume decreases as particle radius increases. The total capillary volume in such a system however is made up of cavities as well as open pores. Calculation of the open pore volume and its relation with particle radius which were omitted in the previous communication (loc. cit.) are presented in this paper.

An Open Pore

By placing four spherical particles in juxtaposition, a cavity and four adjacent open pores are formed. Let all the four spherical particles be of the same radius $r$. The centres of these four spherical particles lie at the vertices of a regular tetrahedron of edge $2r$. The cavity will have four necks which lie in the four faces of the tetrahedron. In continuation of these necks there are the four open pores surrounding the cavity. Such an open pore has a tapering from one end which is wide to the other end which is narrow. In order to calculate the volume of each open pore it is necessary to specify its boundaries. The central part of the open pore is made up of portions of surfaces of the three spheres forming the open pore. On the side where it adjoins the cavity, the open pore ends in the plane of the neck of the cavity and on the opposite side in the plane tangential to the three spheres forming the open pore. The boundary between two adjoining open pores remains to be specified. When all the open pores are completely filled with a liquid, the liquid meniscus in any open pore will be a triangular plane surface (part of the tangential plane above referred to) ending at the three edges with
portions of a cylindrical surface. Every open pore has, in this way, its boundary at the wide end made up of a triangular plane and three bits of a cylindrical surface at the edges.

The Volume of an Open Pore

The volume of an open pore is therefore made up of two parts, (1) the volume $V_1$ bounded by the triangular part of the meniscus, the plane of the neck and the surfaces of the spheres. (2) The volume $3V_2$ included between the spheres and the cylindrical parts of the meniscus.

The volume $V_1$ is the difference between the volume of the right prism obtained by drawing perpendiculars on the common tangent plane (triangular part of the meniscus) from the centres of the three spheres and the volume of the portions of the surfaces of these spheres, lying inside the prism. Hence $V_1 = (\sqrt{3} - \frac{\pi}{3})r^3$.

Let $V_2$ be the volume included between the cylindrical part of the meniscus and the spheres. Of the three such cylindrical parts each is a part of the surface of a complete cylinder of length $2r$ and radius $r$ and the volume included between this cylindrical surface and the surfaces of the two hemispheres which are enveloped by the cylinder $= \frac{1}{6}\pi r^3$. If $2\alpha$ is the angle between the planes of the wide ends of two adjoining open pores, $V_2 = \frac{\alpha}{2\pi} \frac{2}{3} \pi r^3 = \frac{1}{3} ar^3$.

But $2\alpha$ is also the angle between two adjacent faces of the tetrahedron. Therefore $\alpha = \frac{1}{2} \cos^{-1} \frac{1}{3}$ and $V_2 = \frac{1}{6} (\cos^{-1} \frac{1}{3}) r^3$.

There are three such cylindrical portions in each open pore. Hence the volume of an open pore

$$V = V_1 + 3V_2 = \left(\sqrt{3} - \frac{\pi}{3} + \frac{1}{2} \cos^{-1} \frac{1}{3}\right) r^3.$$ 

Total Open Pore Volume

The total number of open pores when there are $N$ spherical particles is to be calculated. At least three spheres are required for the formation of an open pore and by placing them in close contact two open pores are formed. Each additional sphere removes one open pore and adds three giving a net increase of two. Hence total number of open pores $= 2(N - 3) + 2 = 2N - 4$.

Since $N = \frac{r_0^3}{r^3}$, where $r_0^3 = \frac{3M}{4\pi \rho}$

Total number of open pores $= \frac{2r_0^3}{r^3} - 4$
Total open pore volume

\[ V_\phi = 2 \left( \sqrt{3} - \frac{\pi}{3} + \frac{1}{2} \cos^{-1} \frac{1}{3} \right) (r_0^3 - 2r^3) \]

putting \( B = 2 \left( \sqrt{3} - \frac{\pi}{3} + \frac{1}{2} \cos^{-1} \frac{1}{3} \right) \)

\[ V_\phi = B (r_0^3 - 2r^3) \]

Total Cavity Volume

The calculation of the volume of a cavity and the relation between the total cavity volume and the particle radius have been indicated in the previous paper.\(^1\)

Total cavity volume

\[ V_c = \left( \frac{2\sqrt{2}}{3} - 4 \left( \cos^{-1} \frac{\pi}{3} - \frac{\pi}{3} \right) \right) (r_0^3 - 3r^3), \text{ or} \]

\[ V_c = A (r_0^3 - 3r^3) \]

Total Capillary Volume

The total capillary volume \( V \) is made up of total cavity volume \( V_c \) and open pore volume \( V_\phi \).

Total capillary volume,

\[ V = ar_0^3 - br^3. \]

In the above equation \( a \) and \( b \) are positive constants. It is obvious from the above expression that the total capillary volume decreases as particle radius \( r \) increases.

Open Pore Volume in Relation to Cavity Volume

The ratio of the total open pore volume to the total cavity volume is given by

\[ \frac{V_\phi}{V_c} = \frac{\sqrt{3} - \frac{\pi}{3} + \frac{1}{2} \cos^{-1} \frac{1}{3}}{\sqrt{2} + \frac{2\pi}{3} - 2 \cos^{-1} \frac{1}{3}} \]

\[ \frac{r_0^3 - 2r^3}{r_0^3 - 3r^3} \]

putting

\[ K = \frac{\sqrt{3} - \frac{\pi}{3} + \frac{1}{2} \cos^{-1} \frac{1}{3}}{\sqrt{2} + \frac{2\pi}{3} - 2 \cos^{-1} \frac{1}{3}} \]

\[ \frac{V_\phi}{V_c} = K \frac{r_0^3 - 2r^3}{r_0^3 - 3r^3} \]

If \( r \) tends to zero, \( \frac{V_\phi}{V_c} \rightarrow K \).
As particle size diminishes, *i.e.*, as $r$ tends to zero the ratio of the total open pore volume to the total cavity volume tends to the limiting value $K$.

If $r$ tends to $\frac{r_0}{\sqrt[4]{4}}$, $\frac{V_p}{V_c} \to 2K$.

As particle size increases, the ratio increases until when the coalescence has proceeded so far that the whole mass consists of only four spherical particles producing a single cavity and four open pores, the ratio becomes $2K$. This represents the upper limit of the ratio since beyond this stage there can be no cavity.

Calculation of the cavity volume, open pore volume and hence the total capillary volume in relation to particle radius is made assuming a close packing of spherical particles of equiradius. This is not strictly true to random distribution. As remarked in the previous paper (*loc. cit.*), by the substitution of a suitable average value for $r$ the form of the mathematical formulation remains the same and the nature of the relation will not alter. The present mathematical approach of the problem is to be considered as a preliminary to a more rigorous quantitative formulation.

**Summary**

In a system of closely packed spherical particles, formation of two different types of capillaries—cavities and open pores—is indicated.

Assuming spherical particles of equiradius, the volume of an open pore is calculated in relation to particle radius. The total open pore is calculated in relation to particle radius. The total open pore volume just as the total cavity volume, decreases as the particle radius increases.

The ratio of the open pore volume to the cavity volume increases as particle radius increases. The value of this ratio when the particle radius is increased to the maximum limit at which the whole mass consists of four spheres producing a cavity and four open pores is twice the value when the particle radius tends to the limiting value of zero.

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**REFERENCES**