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PORE STRUCTURE OF SOLIDS

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Abstract—A small grain of iron catalyst, used in the synthesis of ammonia, has an external surface of about 1 cm^2/g, but it has an internal surface of 100,000 cm^2/g. Since catalysis takes place on the surface, obviously the surface in the pores is of vital importance. But not all pores are of equal importance; in very narrow pores the diffusion is slow; in large pores the surface is small. The sizes of pores have just as important roles in adsorbents, like silica gel and active carbon, and in other solids, like concrete.

The determination of the distribution of the total pore surface and the total pore volume in pores of different widths is called pore structure analysis. The first methods for pore structure analysis were proposed in 1945; Ritter and Drake used the mercury porosimeter, and Wheeler used nitrogen adsorption isotherms. Subsequently others improved Wheeler's method. Recently we proposed two new approaches for pore structure analysis, both based on adsorption isotherms: one for the analysis of very narrow pores, the micropores, and one for the analysis of the wider pores. The first is the only method proposed for micropore analysis, the second is an improvement on the previous methods for the analysis of wider pores.

When I started my professional life as a junior research chemist 47 yr ago, the first problem I worked on was the mechanism of the synthesis of ammonia by iron catalysts. At that time it was known for many decades that catalytic reactions take place on the surface of the catalyst, but nobody paid any attention to the location of the surface. If one takes a very small grain of iron catalyst which weighs 1 g, the surface that one sees is 1 cm^2. But after we learned how to measure the surface by the adsorption of nitrogen or some other gas, we found that the surface area was not 1 cm^2, but 100,000 cm^2, or 10 m^2. So obviously all of the surface was located inside, in the pores of the catalyst. If the pores are too wide, there is only a small surface in a given volume of catalyst, so we have a poor catalyst. If the pores are too narrow, the diffusion of the reactants to the active centers in the pores or the outward diffusion is slow, so we again have a poor catalyst. But this is not the whole story. The sizes of the pores can influence the order and the energy of activation of the catalytic reaction, the poisoning characteristics, and the temperature and pressure gradients which build up in the catalyst bed. So, obviously, it is important to know how the total surface and the total pore volume are distributed in pores of different sizes, and this is important not only for catalysts but also for adsorbents like silica gel and active carbon, and even for other solids which are neither catalysts nor adsorbents, such as, for example, hardened cement paste, the cementing material in concrete. Such determinations are called pore structure analyses.

When my book on adsorption appeared 32 yr ago, I devoted a long chapter to the pore structure of adsorbents.[1] In that chapter, I proposed a very crude method for pore structure analysis, which I never used, and I only know of one paper in which it was used. But apparently others became interested in the subject, as 2 yr later, in 1945, two good methods were proposed independently, which with various modifications are being used to this date. One of these is the mercury porosimeter method of Ritter and Drake;[2] the other is the nitrogen adsorption method of Wheeler.[3] If I were to discuss these methods in detail, half an hour would not be enough, and I wish to spend most of my time on the two methods that I developed at Clarkson, together with my co-workers and Ph.D. students. Dubinin classified the pores into three groups: micropores, having widths of 16–20 Å or less, mesopores having widths from 20 to 1000 Å, and macropores, having widths of more than 1000 Å. The mercury porosimeter is good for the analysis of the larger mesopores and macropores, but most of the surface is in the micropores and the smaller mesopores. Wheeler's method is good for mesopores, but not for the micropores. Our two methods enable us to perform a complete pore structure analysis, with the exception of the smallest micropores, which we called ultramicropores, i.e. pores on the walls of which only a single layer of molecules can be adsorbed.

Both of our methods depend on gas adsorption, so I have to say something about the older gas adsorption methods first. Figure 1 shows some imaginary isotherms of nitrogen at 77°K, its boiling point. Disregard Curve 1, a Type I or Langmuir type of isotherm; we will not discuss this. Curve 2 is supposed to represent a Type II isotherm on a nonporous solid. Point B represents the monolayer, and the isotherm is for multilayer adsorption. Curves 3 and 4 represent the adsorption and desorption isotherms respectively of a porous solid. This has the same surface area as Curve 2, as shown by the fact that they both have the same Point B, but there are two differences between the isotherms. One is that beginning at a relative pressure of about 0.4, the porous adsorbent has more adsorption than the nonporous adsorbent; the other is that the porous adsorbent has a hysteresis loop, ending at a relative pressure of 0.4. Both of these effects are attributed to capillary condensation, on top of the multilayer adsorption. This capillary condensation is used for the pore structure analysis.

The isotherm is divided into parts, for example pores which fill up by capillary condensation between relative pressures of 0.4 and 0.45, 0.45–0.5, and so on up to close to the end of the isotherm; and the three pore parameters, the volume, the average radius, and the surface area are evaluated for each pore group. One must use an idealized pore shape, which is usually the cylinder; occasionally the pores are assumed to be parallel plates. Now please look at Fig. 2. I said that capillary condensation starts at a relative pressure of 0.4, but before that pressure is reached, there is an adsorbed film on the pore walls. This is shown by the broken lines in the figure. Between the

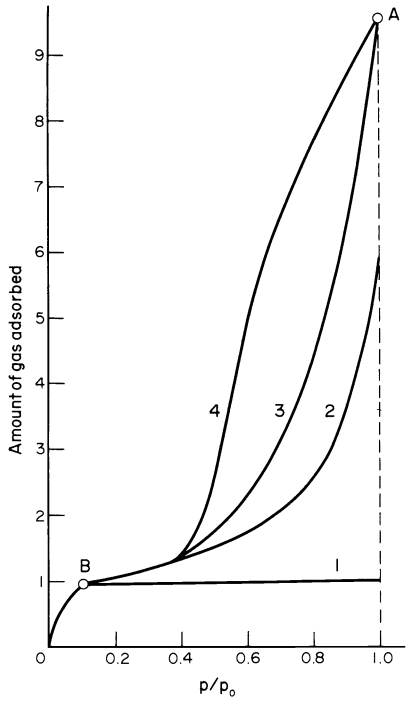

Fig. 1. Imaginary nitrogen isotherms at 77°K. Curve (1) a Type I isotherm. Curve (2) a Type II isotherm of a nonporous adsorbent. Curves (3, 4) adsorption and desorption isotherm of a porous adsorbent.

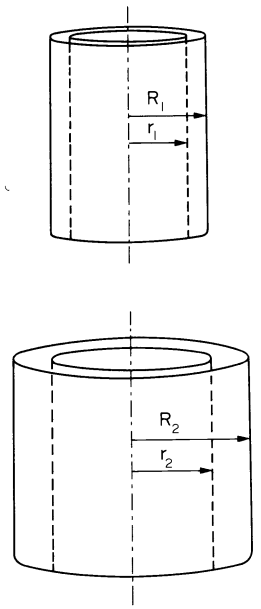

Fig. 2. Cylindrical pores with adsorbed films on the pore walls. L.c. r_1 and r_2 represent the radii of the cores, and capital R_1 and R_2 represent the radii of the pores.

adsorbed films, there is an empty space, which I called the core of the pore. The radius of the core is r, and as you see, capillary condensation takes place in the core of the pore. The Kelvin equation is used to evaluate the radius of the core:

$$RT \ln \frac{p}{p_s} = -\frac{2\gamma V}{r}$$

where p/p_s is the relative pressure, γ and V are the surface tension and the molar volume of the adsorbate, assumed to be equal to that of liquid nitrogen, and r is the radius of the core. If one assumes that the pores are parallel plates, the same Kelvin equation applies, except that r is not the radius of the cylinder but the distance between the plates. Now if we use the Kelvin equation, we calculate r by substituting 0.4 and 0.45 for p/p_s, and the arithmetic average of the two r values is the average radius of the smallest group of cores. The excess adsorption over the multilayer adsorption, which is the capillary condensation, gives the volume of the core group. Knowing the average core radius and the core volume, we can calculate the surface of the cylinder, which is the surface of the core group. We then do the same calculations for the next larger core group, in which capillary condensation takes place between relative pressures of 0.45 and 0.5, and so we proceed along the isotherm to larger and larger core groups.

We have now the three core parameters, volume, surface, and average radius for each group; the next step is to obtain the pore parameters. In order to do that, we must add the thickness of the adsorbed film to the radius of the core. In nonporous adsorbents, like the one illustrated in Curve 2 in Fig. 1, there is no capillary condensation, so the thickness of the adsorbed film can be calculated at each relative pressure, and this is added to the core radius in the porous adsorbent. Thus the radius of the pore is capital R in Fig. 2, and the pore volume and surface are the volume and surface of this larger cylinder. All this is older work, but I had to tell you about it to make our first contribution to pore structure analysis understandable.

Please notice that in all older methods only one core parameter was experimental, i.e. taken from the isotherm, namely the volume. Then, because one had to assume a pore shape, one obtained two fictitious core parameters: the radius and the surface. We used a method in which all three core parameters were experimental.[4] The volume of the core was obtained from the isotherms, as in the older methods, so it was experimental. But the surface was also obtained from the isotherm. For this we used a modification of an equation developed by Kiselev.[5] Consider a pore of any irregular shape, the walls of which are covered by an adsorbed film. When capillary condensation takes place in the core, the surface disappears, and the free energy change in this process is $\gamma\, ds$, where γ is the surface tension and s is the surface area. At the same time, a certain amount of gas disappears from the gas phase and liquefies in the core. The molar free energy change in this process is $RT \ln (p_s/p)$, and the number of moles of gas which liquefy is da. Integrating and solving for the surface, we obtain

$$s = \frac{1}{\gamma} \int_{a_{0.4}}^{a_{0.45}} -RT \ln \frac{p}{p_s} \cdot da.$$

The limits of integration are the moles of gas adsorbed at relative pressures of 0.4 and 0.45. One then proceeds to the wider group, with relative pressures of 0.45–0.5, and so on.

Finally, we performed our pore structure analysis not in terms of the Kelvin radius, as others did, but in terms of the hydraulic radius, V/S, the ratio of the core volume to the core surface. This is a sort of average dimension for the width or radius of irregular pores. Since both the volume and surface were experimental, the hydraulic radius was also experimental. Thus, in place of one

experimental core parameter, our method used three experimental core parameters.

However, if one wishes to proceed from cores to pores, one must assume a pore shape. This is illustrated in Fig. 3. Here Curve 1, the small solid curve, is the core volume distribution, assuming no particular model. Within that is the broken Curve 2, to which we applied certain corrections, so we call it the corrected curve without model. You see that it is quite similar to Curve 1, and we use it only if we want to proceed to pore distribution curves. Curve 3 gives the pore volume distribution if we assume that the pores are cylindrical, and Curve 4, if we assume that the pores are parallel plates. The two curves are different, but not very different.

Now you may ask that if we finish with cylindrical or parallel plate pores, why don't we do it right at the start, as everybody else did. There are several answers to this. In the first place, in industrial operations one could use the core structure analysis, which is completely modelless, in place of pore structure analysis. In the second place, we showed in a paper that if one has only one experimental core parameter, the volume, one can go very far wrong in the calculation of the surface, whereas if all three core parameters are experimental, one cannot go far wrong whether one uses parallel plate, cylindrical or spherical pore shape idealizations.[6] The third reason requires some introduction.

How can one tell whether our pore structure analysis is correct? After the analysis is completed, one can add the surfaces of all pore groups and thus obtain the cumulative pore surface. In all older methods, the investigators compared this with the BET surface, and if the agreement was good, they considered that their analysis was correct. We added to this criterion a second one; namely that the cumulative pore volume had to agree with the volume adsorbed at the saturation pressure of the adsorbate, p_s. Earlier investigators could not use this second criterion, because the Kelvin radius is infinite at the saturation pressure. So they had to stop at a lower relative pressure, for example, 0.93. Thus the largest pores were left out of consideration. In these pores, the surface is small but the volume is large, so they could not use the volume criterion. By using the hydraulic radius instead of the Kelvin radius, we could cover the entire isotherm, so we could use both criteria. Of course, even though in my figures I show only pore volume distribution curves, one can just as easily plot pore surface distribution curves.

I could say a lot more about this subject, but that would leave me no time for the discussion of our second contribution, the analysis of micropores. There was no method proposed before ours for micropore analysis. I remind you that these are pores with radii of 16–20 Å or less. Some very important adsorbents contain only micropores, and very many others contain micropores and mesopores. In micropores there is no capillary condensation because meniscus cannot form in such small pores, so the method that I will describe is quite different from the methods I have described so far.

To start with, I remind you how we corrected the core dimensions to pore dimensions by adding the thickness of the adsorbed film to the radius of the core. Various investigators chose a number of nonporous adsorbents, determined their nitrogen isotherms, and constructed an average isotherm. The adsorbed film was considered a liquid, so at each relative pressure the amount adsorbed was converted into an amount of liquid adsorbed; this was then divided by the BET surface, and thus they obtained the statistical thickness of the film at each relative pressure. Then one can plot the volume adsorbed against the statistical thickness, t, and a t-curve is obtained,

$$t = 10^4 v_l / S_{BET}$$

where if v_l is expressed in milliliters and S_{BET} in m^2/g, then t is obtained in Å. This t-curve is then used for the corrections I discussed before.

You see that the equation is a straight line, because S_{BET} is a constant, which can be evaluated from the slope.

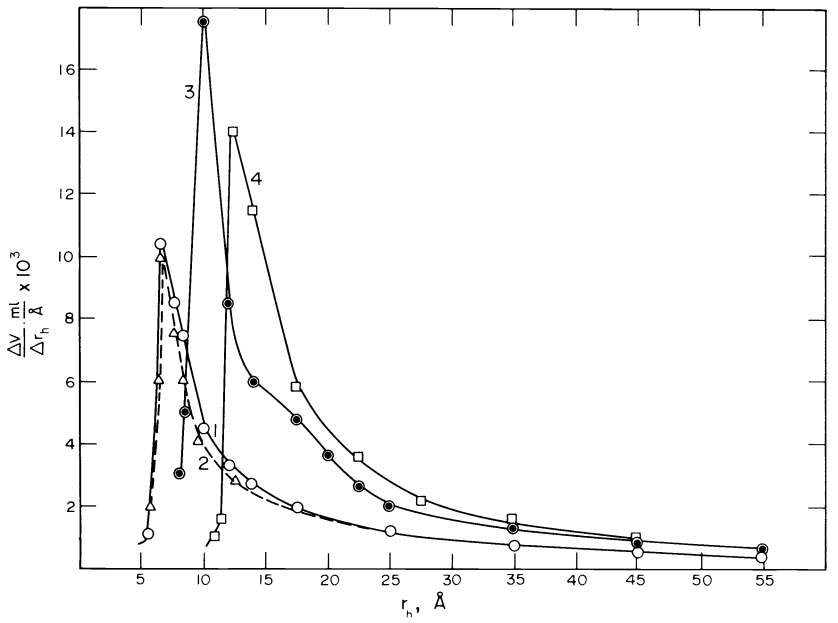

Fig. 3. Pore volume analysis curves. Curve (1) analysis of cores (completely modelless). Curve (2) corrected analysis of cores. Curve (3) pore volume analysis with cylindrical idealization. Curve (4) pore volume analysis with parallel-plate idealization.

Lippens and de Boer[7] called the slope S_t, since it is obtained from the t-curve, and it is usually quite close to S_{BET}. Now Lippens and de Boer argued in the following way. On a nonporous adsorbent, there is only multilayer adsorption, and so the t-curve is a straight line from zero pressure to the saturation pressure. This must be so, because the equation is really an identity. If, however, capillary condensation starts, the points in the t-curve deviate upwards, because of the additional adsorption. On the other hand, if very narrow pores become filled with adsorbate, the points deviate downwards, because some of the surface becomes unavailable for further adsorption. We used these downward deviations of the t-curve for our micropore analysis method, which we abbreviated to MP-method.

Let us look now at Fig. 4, which gives the adsorption isotherm for a silica gel, which contains only micropores.[8] It is a completely reversible Type I isotherm; the empty circles are adsorption points and the filled-in circles desorption points. We convert this isotherm into a v_l-t-curve, which is shown in Fig. 5. Each adsorption point is converted into volume of liquid adsorbed, which gives the ordinate, and instead of plotting the relative pressure as abscissa, as in an adsorption isotherm, we plot the thickness of the adsorbed film as abscissa. Thus we obtain a straight line, as we should, and this is Curve 1. The slope of this gives S_t, the surface area of the silica gel, which in this instance is 792 m^2/g, while the BET area is 793 m^2/g. This is an exceptionally close agreement; we do not expect such close agreement ordinarily. Now look at the next curve, Curve 2. Between film thicknesses of 4.0 and 4.5 Å, the curve begins to deviate downward, because the volume of some of the smaller pores is filled up, and so a smaller surface is available for further adsorption. The slope of Curve 2 gives the surface which remains for further adsorption, so $S_1 - S_2$ gives the surface which disappeared while the volume of the smaller pores filled up with liquid. Since the downward deviation began between 4.0 and 4.5 Å, the average thickness is 4.25 Å, and the volume which disappeared, i.e. the volume of the first and smallest micropore group is in milliliters

$$v_l = 10^{-4}(S_1 - S_2)\left(\frac{t_1 + t_2}{2}\right).$$

Thus we have the volume, surface, and average width of the first pore group, so we can proceed to the next. In the end we obtain the pore volume distribution curve shown in Fig. 6. The abscissa is the hydraulic radius, which for parallel plate pores is half the pore width; so Fig. 6 shows that the maximum of the pores is at 9 Å, and the end is somewhat less than 16 Å, showing that all pores in this silica gel are micropores.

But how do we know that this analysis is correct? We mentioned our two criteria before: the cumulative pore surface must agree with the BET surface, and the cumulative pore volume must agree with the volume adsorbed at the saturation pressure. But unfortunately we cannot use these two criteria. We immediately saw that the nature of the analysis is such that the cumulative surface must agree with the BET surface, so we could not use this criterion. Later Dubinin showed that the cumulative pore volume must agree with the volume adsorbed at the

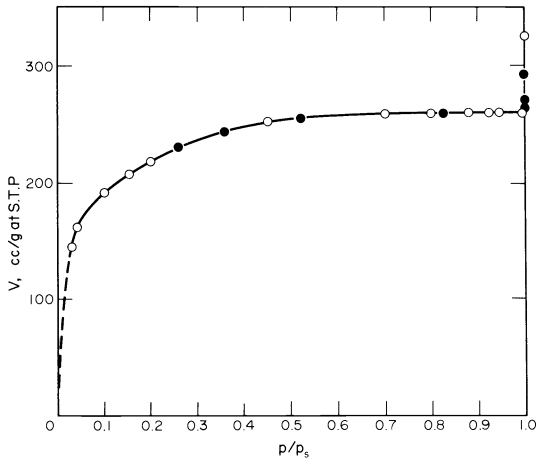

Fig. 4. Adsorption isotherm of a silica gel which contains only micropores.

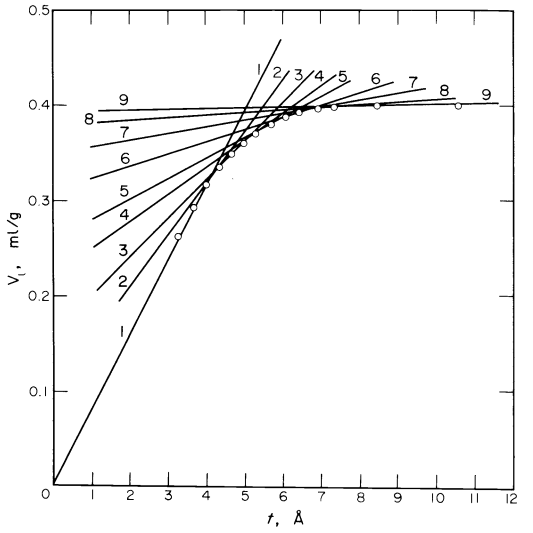

Fig. 5. The same isotherm as in Fig. 4, converted into a $v_l - t$ plot.

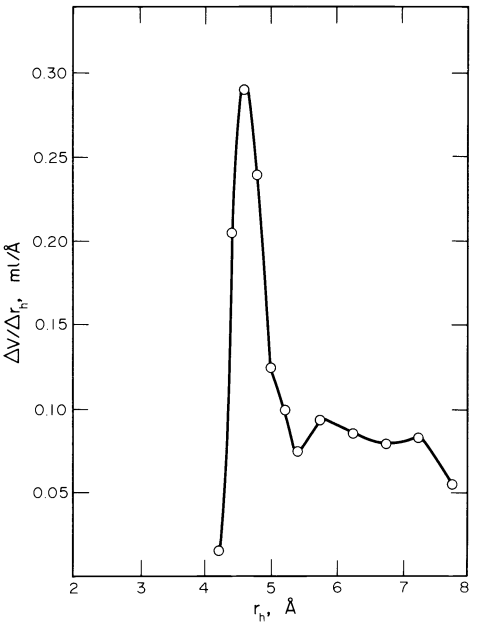

Fig. 6. Pore volume analysis curve of the isotherm shown in Fig. 4.

saturation pressure, so we could not use that criterion, either.[9]

So where are we? The situation is not as hopeless as it seems; in fact, it is not hopeless at all. I will use an argument which consists of three steps. Let us look at Table 1. Here are the results for two silica gels, which contain no micropores. So the total analysis was performed by the method described by me earlier. We used four isotherms for the analysis of each silica gel: nitrogen at its boiling point, water vapor at 25°C, and oxygen at two temperatures: at its boiling point and at the boiling point of nitrogen.[10] In the first column, the cumulative pore surface results are given for one of the silica gels; under this is the average of the four values, then the BET surface obtained by nitrogen, and finally the difference in per cent. The second column gives the same for the other silica gel, the third and fourth columns give the volume results for the two silica gels. They are well within the experimental errors; the average of the four differences is 1.3%. So both the surface and volume criteria are excellently satisfied, and the conclusion is that the analysis of the wide pores is correct.

Table 1. Comparison between cumulative pore surfaces, obtained from four isotherms, with S_{BET}, and comparison of cumulative pore volumes with v_s. The two silica gels, D-59 and D-81 contain no micropores

	D-59 S_{cum}	D-81 S_{cum}	D-59 V_{cum}	D-81 V_{cum}
N_2	277	411	1.128	0.782
H_2O	280	393	1.084	[0.822]
O_2 (77°)	280	393	1.075	0.744
O_2 (90°)	285	404	1.128	0.748
Average =	280	400	1.104	0.758
S_{BET} (N_2) =	273	399	V_s = 1.088	0.751
Difference =	2.5%	0.25%	1.5%	0.9%

The second step in the argument is to look at two silica gels which have both micropores and wider pores, mostly mesopores.[11] Now obviously the cumulative surface in the micropores cannot be equal to the BET surface, because the cumulative surface in the micro and mesopores must be equal to the BET surface, and the cumulative pore volume in the micropores cannot be equal to the volume adsorbed at the saturation pressure, because the cumulative pore volume in the micro and mesopores must be equal to the volume adsorbed at the saturation pressure. So we performed pore structure analysis for the two silica gels, using the two methods I described, one for the micropores and one for the wider pores. The results are shown in Table 2. The third column in the first row shows the cumulative pore surface in the micropores, and the fourth shows the cumulative pore surface in the wider pores. The volume results are below. For the first gel 90% of the pore surface and only 19% of the pore volume was in micropores; for the other gel, 73% of the pore surface and 33% of the pore volume was in micropores. But the totals for the gels are in excellent agreement with the two criteria; the average of the differences in this case is only 1.4%. So we conclude that adsorbents with both micropores and mesopores satisfy the two criteria of correctness excellently; thus their pore structure analysis is correct.

Table 2. Comparison of cumulative pore surfaces and pore volumes with S_{BET} and v_s. The two silica gels, SB and SL, contain both micropores and wider pores

	Pore structure data			
Gel	S_{BET}	ΣS_m	ΣS_w	S_{total}
SB	396	355	43	398
SL	658	475	173	648
Gel	V_s	ΣV_m	ΣV_w	V_{total}
SB	0.788	0.152	0.644	0.795
SL	0.703	0.215	0.469	0.684

The conclusion from the two-step argument used so far is that since our method is correct for wide pores, and since our two methods jointly are correct for mesopores and micropores, it follows that our micropore analysis method is correct for adsorbents with mixed pore systems. And now comes the third step in the argument. The two criteria of correctness of analysis do not apply to adsorbents which contain only micropores. Nevertheless, if our micropore analysis method is correct for adsorbents which have mixed pores, we do not see any reason why the method should be incorrect for adsorbents which contain micropores only. This is the weakest point in my argument, and if someone comes along with a good reason against it, I will accept it; but until then I will remain satisfied with our micropore analysis method.

Our two methods jointly make a complete pore structure analysis possible for the overwhelming majority of porous solids, which none of the earlier methods could do. Our methods fail, as I mentioned before, for such adsorbents which contain predominantly exceedingly narrow pores, such as, for example, certain zeolites.

There are numerous important aspects of pore structure analysis, which I could not discuss in the short time available. The figures are used only as examples; we have analyzed about 50 adsorbent–adsorbate systems, and published about 20 papers on the subject.

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