MICROPOROUS MEDIA

Synthesis, Properties, and Modeling

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To my mother, Tamara Slavkin

Preface

This book is directed not only to specialists in interface science and porosity but also to graduate students and scientists having a strong background in natural sciences and interested in more knowledge about porosity and especially microporosity. Each chapter starts with a brief overview of well-known facts and concepts, then more significant matters are analyzed with recommendations and conclusions, and then we present examples of original, specific scientific and technical ideas. Thus, the reader can find in this book all kinds of information related to microporosity—from the general to very specific ideas. Of course, most references are not discussed in detail, because this is not a handbook.

WHAT IS A PORE?

A *pore* can be understood as a void inside a solid structure or solid material. A solid material containing pores is called *porous material*.

Porous structures are widespread around us. What solid materials are porous? This question needs too long an answer. It is much easier to list solid materials that cannot be considered porous: most crystals (comprising metals and their alloys, diamond, ionic salts, etc.), some special plastics, and special ceramics. Hence, it is not an error to claim that most existing materials are porous.

Let us list some widespread porous materials:

All noncrystalline solids found in nature
Concretes and most ceramics and composites

Rubbers and other polymers
All foams
Active carbon (also called *activated carbon*), zeolites, silica gel, alumina gel, and most other heterogeneous catalysts
Glasses
Metallic foams

Is the role of pores in our life positive or negative? That depends on the situation. High porosity may catastrophically reduce the mechanical stability of constructive materials, their resistance to corrosion and erosion. On the other hand, this fact allows the regulation of mechanical and chemical resistance of a material without any change in its chemical composition. Pores intensify all heat- and mass-transfer processes in solid phase. Even our body's tissue is porous; otherwise, it could not provide the variety of heat- and mass-transfer processes needed for our life.

The preceding analysis is relevant for visible pores, i.e., macropores, the properties of which are determined first of all by two factors: the total volume fraction of voids (porosity of the structure ξ) and their total surface (internal surface of a porous material). However, for very small pores (nanopores, the characteristic size of which is below $500\,\text{Å} = 50\,\text{nm}$), not only porosity and internal surface are important for the determination of properties. For such small pores, quantum effects related to the interactions with the pore walls become so significant that they increase the total internal energy of the solid phase. This causes serious changes in properties of the porous media such as chemical reactions, adsorption, specific capillary effects, etc. Thus, for the case of nanopores we need to take into account not only porosity and internal surface but also the total internal energy and energy distribution of nanopores in the considered structure.

Nevertheless, even nanoporosity is not the limiting size for the variety of properties of the internal volume of solid structures. In nanopores below 20 Å (2 nm) a very strange phenomenon occurs: their internal surface is not as important as their internal volume—the volume of very narrow nanopores, named *micropores*. The energy of micropores is so high that many measurable properties of solid materials are determined first by the energy of the microporous substructure. For example, it is well known that carbon is hydrophobic ("repulses" water). Active carbon has approximately the same chemical composition as ordinary carbon; hence, active carbon should also be hydrophobic, obviously. However, due to the high energy of micropores, active carbon has the ability to adsorb water—as if this material was hydrophilic ("attracting" water).

Thus, we obtain a paradox: measurable properties of many existing materials can be determined by micropores—invisible empty fragments of solid structures. Two solid samples having the same chemical composition may seem absolutely identical except for differences in their measured density, but differ in their properties—due only to micropores!

The exceptional properties of microporous materials determine their uses. Let us note some of them.

PROPERTIES AND USES OF PORES

Electrical and thermal insulation. Most existing microporous materials are very effective as electrical and thermal insulators. If necessary, their electrical and thermal resistance can be increased up to that of air, and even further, because air can eventually be ionized (which makes it electrically conductive) or have mechanical motion (which provides convective heat transfer).

Let us notice that in some cases we need conductive microporous materials, which is an unusual situation, but such materials can be synthesized (e.g., polymer electrolytes for lithium batteries).

Separation processes. All microporous materials can be used for certain processes of fluid mixture separation. Inside micropores there are two principal mechanisms allowing separation: adsorption and selective separation, both related to the exceptional properties of micropores.

Adsorption is a process of preferable fixation, in which gas or liquid molecules are captured by micropores; after the rest of the fluid is removed, the adsorbed substance can be delivered from the solid phase by heating and/or pressure decrease. For example, if we want to separate a water–oil mixture, it is enough to ensure its contact with active carbon; there the oil is adsorbed (you may be reminded that, as was mentioned earlier, water is also adsorbed; this is true, but if carbon micropores have a "choice," they preferably adsorb the organic phase), the water is separated, the carbon is heated, and oil purified from water is delivered.

A special sequence of the adsorptive properties of microporous materials is involved in their *catalytic activity*. Adsorbing some substances, the internal surface of microporous catalysts becomes the zone of complex chemical reactions. Such *heterogeneous catalysis* is the base of modern chemical technology. In several situations, adsorption of reagents in micropores may even change the result of the reaction.

Selective separation takes place in very special microporous structures (molecular sieves), the pore size of which is below 7 Å (so-called ultramicropores), in such materials as zeolites and some kinds of active carbon, silica, or alumina gel. The selection is due to several factors, including the effective size of the separated particles and their interactions with the material of the micropore walls. The simplest example is an organic polymer, which can be removed from water in a zeolite due to not only the small size of molecules of water but also because of the preferable interaction of water with zeolite, whereas macromolecules, so big for ultramicropores, are repulsed by the zeolite material. The selective properties of ultramicropores are the basis for membranes used for water purification and other separation processes.

Military uses. The opportunity to regulate the mechanical properties of solids offers some military applications. It is well known that multilayer protection of "steel + microporous ceramics + steel + microporous ceramics..." is more effective against explosions than simple steel of the same weight. That is due to the specific interactions of microporous structure with the explosion wave.

Sanitary and medical uses. The ability of microporous materials to selectively adsorb organics finds applications in health protection. For example, such microporous materials as active carbon and silica gel are used in gas masks for protection from poison and aggressive gases and vapors. The undesired gas is adsorbed by the microporous material and cannot harm anyone.

A similar application of the same materials is found in the pharmacy. Tablets of active carbon and/or silica gel adsorb nonappropriate products of metabolism in the human organism, which are then easily removed.

FORECASTING PROPERTIES OF MICROPOROUS STRUCTURES

Since micropores are so important for us, it seems very attractive to deduce all the characteristics related to microporosity from several predictable factors, such as conditions of material preparation (synthesis). This is the main purpose of this book: the investigation of the relationship between the conditions of synthesis of a porous (microporous) material, its structural parameters, and its measurable properties—properties such as adsorption, percolation, permeability, and mechanical resistance. Of course, the conditions of the synthesis determine the structure of the product (microporous material), whereas its structure determines all properties that could interest the researchers.

In the light of our main objective, we analyze the existing models of micropores and microporosity-related phenomena, particularly their usefulness for forecasting the technical merit of new materials—meaning materials just designed in laboratories.

METHODOLOGY OF MODELING MICROPOROSITY

Modeling of microporosity is extremely complicated because of the combination of quantum effects inside the micropores with the rich variety of shapes and large spectrum of characteristic sizes of micropores. Therefore, traditional methods of modeling the condensed phase are not applicable to microporosity. A possible solution is the use of modified statistical nonequilibrium thermodynamics. Such an approach allows the solution of some problems related to microporosity. Such a modified thermodynamic approach is applicable not only to modeling microporous structures but also to the simulation of very special phenomena, such as the beginning of the universe by the Big Bang and the beginning of life (this aspect is analyzed in Appendix 2).

STRUCTURE OF THE BOOK

The goals outlined above determine the structure of this book.

Chapter 1 presents general concepts regarding microporosity and the most important definitions. The classification of pores and micropores is given. Several methodological problems (classification of models of porosity, the similarity and divergences between *micropore* and *defect in crystal*, similarity and differences between adsorption in macro-, meso-, micropores and absorption, etc.) are analyzed. Most of the important concepts are defined and explained.

Chapter 2 focuses on the analysis of experimental methods for the study of microporous media: techniques used, problems solved, and errors of measurement and secondary problems that appear because of "intervention" in the microporous structure.

Chapter 3 presents the theoretical aspect of pore formation. Typical processes for porous material synthesis, together with their mathematical models, are considered and compared. The relationship between preparation conditions and the characteristics of the obtained microporous structure is always the central point. Such problems as "chemical" properties of pores, fractal formation, and branched structure formation are discussed. We analyze the specific features of the methodology of microporous media, in comparison with traditional methods of study of condensed matter.

Chapter 4 contains the analysis of properties of microporous structures: adsorption and desorption, percolation, permeability, and mechanical resistance. These properties are analyzed without specifying the structural parameters.

Chapter 5 discusses the existing models of microporous structure. Existing models are classified, compared, and analyzed. Most attention is paid to the fractal model, the thermodynamic model, and the polymeric model: their applicability and shortcomings, the opportunities they offer for combination, etc. The relationship of synthesis–structure–measurable properties is analyzed throughout.

Chapter 6 presents the engineering applications of models of microporosity. The theoretical results discussed in Chapters 3 to 5 are transformed to calculative techniques available for engineers, with energetic, technical, and economic estimations.

Chapter 7 offers the perspectives for the further development of the concept of microporosity, analyzing experimental research, and linking it to the relevant theoretical models. The opportunities for the development of theoretical models are considered. Some recommendations regarding investment policy in porous material studies are presented.

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Freddy Romm

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