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A Phenomenological Theory of Diffusion in Heterogeneous Media and Its Use in Describing Membrane Separation Processes

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Within the framework of a unified methodical treatment a critical analysis is given of different methods for the phenomenological description of the processes of the gas permeability of heterogeneous media: lamellar, dispersion type, containing individual inclusions, etc. The introduction of a continuous geometrical factor allows generalised expressions for the effective transport parameters to be obtained. Mathematical modelling methods are used to check the adequacy of the mathematical apparatus considered. The prospects for a directed choice of the structure of the material for controlling the efficiency and selectivity of a gas-separating membrane are investigated.
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I. INTRODUCTION

Composite materials are today being more widely used in membrane technology. A targetted search for such materials requires the development of a systematic approach to the construction of membranes which possess a given efficiency and selectivity using substances with known diffusion properties.

The aim of this review is to consider the prospects for using the steric and chemical organisation of a heterogeneous material to control the parameters of a gas-separating membrane. Consideration is given primarily to an analysis of the current phenomenological theories of diffusion in heterogeneous media and to mathematical modelling of the permeability of various types of such media. Recommendations are given for selecting the topology of the composite material which will provide the required transport properties for the membrane.

II. TYPES OF HETEROGENEOUS STRUCTURES AND THE MAIN APPROACHES TO THE DESCRIPTION OF DIFFUSION IN HETEROGENEOUS MEDIA

The methods for setting up the mathematical apparatus for diffusion in heterogeneous media are determined by the types of structure of the heterogeneous materials.[1-3]

In a "macroheterogeneous" medium which includes non-uniformities of structure comparable with the length of the diffusion wave, there is a distinction between the mechanisms of sequential diffusion (diffusion in a lamellar membrane, in which planar non-uniformities of structure are orientated perpendicular to the direction of flow[4]), parallel diffusion (diffusion along channels isolated from each other and orientated along the direction of flow[5]), dissociative diffusion (diffusion along interpenetrating networks of defects; this can be regarded as parallel diffusion along interconnected channels between which there is reversible exchange of the atoms of the diffusant[6-8]), and the mechanism by which the diffusive flow passes round individual large obstacles of a specific shape and dimensions.[2,9-12] The phenomenological theory of mass transport in media of this type is fairly well developed (see, for example, Refs.1, 15). One exception is the problem of transport in materials containing individual large inclusions, a general solution of which is at present unknown. For such systems there are also no methods for calculating the effective coefficients of permeability and diffusion.

The main class of "microheterogeneous" structures is made up of dispersion media, i.e. solids containing a dispersion of inclusions of a specific shape and size which have different thermodynamic and kinetic properties from the base material. A phenomenological theory of transport in dispersion media was proposed by Maxwell (see Ref.14) to describe the electrical conductivity of dispersions[15-18] and then adapted to the problems of thermal conductivity[19] and diffusion.[20,21] In this model a calculation is first made of the perturbations of the lines of diffusion flow caused by an individual obstacle of a given shape (its dimensions are postulated to be much smaller than the thickness of the specimen) situated in an inifinite homogeneous medium and then the sum is taken of all the perturbations caused by an ensemble of inclusions of the same shape arranged in a specimen of infinite size. In early work this treatment was used to describe diffusion in dilute dispersions but subsquently it was developed as applied to concentrated dispersions and the orderly packing of inclusions of phases of a different nature.[5,22-27] This theory was used to describe diffusion in media containing inclusions with a simple geometrical form: a sphere, plate, cylinder, ellipsoids of rotation, etc. Unfortunately it does not take into account the possibility of a discontinuity in the concentration profile at the boundary between the inclusion and the enclosing medium. The model has a great number of variants and, depending on the method used to sum the perturbations, it leads to different expressions for the effective permeability constant. Up to the present there has been no success in using this theory to describe non-steady-state diffusion.

A model for diffusion in dispersion media which was developed independently[28,29] was first proposed to describe the kinetics of adsorption by biporous sorbents and later to describe the process of sorption of vapours by filled polymers.[30] Within the scope of this theory the kinetics of non-steady-state diffusion from the surrounding medium into a specimen of a specific shape containing identical

inclusions (the shape of the specimen and the inclusions is made arbitrary but simple: a sphere, cylinder, or plate), the dimensions of which are considerably smaller than the length of the diffusion wave, are discussed. Linear and non-linear situations were analysed and expressions given for the initial statistical moments from the kinetic curve, so permitting estimates of the effective diffusion coefficients to be obtained.[31] A significant limitation of this treatment, severely restricting its range of application, is the requirement that the diffusion coefficient in the inclusion be much smaller than the diffusion coefficient in the base material of the specimen.

It would appear that a description of diffusion in a dispersion of point defects can be obtained from the models discussed above by simply reducing the size of the inclusions. However, in practice the theory of diffusion in defect media was developed quite independently by adapting the mathematical machinery which describes diffusion accompanied by a chemical reaction between the diffusant and the solid. Thus, diffusion with temporary retention of the diffusant in the defects (reversible capture in the traps) is interpreted as a reversible first-order chemical reaction,[32,33] diffusion with permanent capture as an irreversible first-order chemical reaction,[34] and diffusion with capture in defects of limited capacity (i.e. diffusion with adsorption at the defects which formally obey the Langmuir isotherm) as a second-order chemical reaction.[35,37] In earlier work dilute dispersions of defects were considered and then a conversion made to essentially heterogeneous media.[38,39] This approach has been fairly well developed so far: the appropriate equations for Fick's first and second laws have been rigorously set down, the formulae for describing non-steady-state mass transport obtained, and the expressions for the effective diffusion coefficients given. For example, the expression for the effective diffusion coefficient in a concentrated dispersion of point defects takes into account the diffusion coefficients both in the enclosing medium and at the defects and also the occurrence of different types of sorption isotherm in the inclusions and in the main component of the medium.[39]

A special class is formed by structures generated from dilute dispersions of point inclusions when the volume fraction of the latter is increased (for brevity in the present work we shall call such heterogeneous substances percolation-type structures[40,41]). The importance of such structures is due to their flexibility which allows conversion from one of the types of structure discussed above to another.

In fact, dispersion of point defects occurs at low concentrations of the inclusions. As their concentration increases the point inclusions are joined together in extended formations (clusters) and the dispersion is characterised by functions for the size and shape distribution of the clusters. In spite of the random nature of the cluster formation this type of dispersion medium obeys strictly defined statistical rules and the evolution of the system can be quantitatively described in terms of percolation theory using such concepts as the percolation threshold and the critical index.[42] At a certain value of the volume fraction a continuous cluster is generated (there is "puncturing" of the membrane accompanied by a sharp change in the transport properties of the membrane). In this case, direct transfer is impossible along any of the components of the heterogeneous structure (an analogue of a lamellar medium). When the volume fraction of the new phase is increased further reversal of the phases takes place, i.e. the old phase now forms inclusions in the new.

It is clear that, depending on the volume fraction of the inclusions, diffusion in a percolation-type medium can be described as "chemical" diffusion, diffusion with reversible capture, diffusion in a dispersion medium, dissociative diffusion, or dispersion in a lamellar medium. A unified description of the evolution of the system from a diffusion point of view requires the percolation theory to be amalgamated with the equations for non-steady-state transfer. However, this course involves serious difficulties. In its current form the percolation theory requires the complete absence of transport along one of the components of the medium and is used only to describe steady-state conditions of permeability.

To sum up this short analysis of known models for diffusion in heterogeneous media the following comments can be made.

(1) There are two main approaches to setting up the mathematical machinery. The first is based on replacing the heterogeneous medium by a homogeneous medium with the same effective diffusion properties. This replacement can be made if the characteristic size of the non-uniformities in the structure is smaller than the length of the diffusion wave. The second approach is used to describe diffusion in media containing individual large inclusions whose size clearly exceeds the length of the diffusion wave. In this case account is taken of the spatial arrangement of the components of the medium, the local values of the coefficients of solubility and diffusion in each component, the shape and size of the inclusions, and also the diffusion resistance of the phase boundary.

Unfortunately up to now these two methods of describing diffusion in heterogeneous media have been developed quite independently of each other. Moreover, even within the framework of a single approach there have arisen different variants which start from almost the same physical principles but lead to different final expressions. For example, depending on the method chosen for averaging the concentration field, the permeability constant P of a dispersion of inclusions is given by the formulae:[1,27]

$$\frac{P}{P_1}=\frac{P_2+2P_1-2\Phi_2(P_1-P_2)}{P_2+2P_1+\Phi_2(P_1-P_2)}$$

where Φ_1 and Φ_2 are the volume fractions and P_1 and P_2 the permeability constants of components 1 and 2 respectively;

$$\frac{P}{P_1}=\frac{P_2+2P_2-W-\Phi_2(2P_1-2P_2-W)}{P_2+2P_2-W+\Phi_2(P_1-P_2+W)}$$

where $W = 0.78(P_2 - P_1)^2/(2P_1 + P_2)$; or

$$P_1P^3-3P_1P_2P^2+(3P_1P_2^2+(P_2-P_1)^3\Phi_1^3)P-P_1P_2^3=0$$

$$2P^2+[P_2-2P_1-3\Phi_2(P_2-P_1)]P-P_1P_2=0$$

$$\left(\frac{P}{P_1}-1\right)=3\Phi_2\left[\frac{P_2+2P_1}{P_2-P_1}-\Phi_2+\frac{\beta(P_2-P_1)\Phi_2^{10/3}}{P_2+(4P_1/3)}+\ldots\right]^{-1}$$

where for simple cubic packing of spheres $\beta = 0.523$ [15] (in Ref.23 $\beta = 1.31$), for body-centred cubic packing of spheres $\beta = 0.129$,[23] and for face-centred cubic packing $\beta = 0.0752$.[23]

An analysis of these expressions shows that they give approximately the same results if $P_2 < P_1$ but considerably different results if $P_2 > P_1$.

With such a diversity of expressions a natural question arises: which of these formulae is most valid physically and universal? Below, by analysing the known models within the framework of a single methodological approach, we shall discuss diffusion in various types of heterogeneous media (dispersion, lamellar, containing individual inclusions, etc.) and shall show that the modified Maxwell equation generated as a result of this analysis allows almost all the known methods of describing diffusion in heterogeneous media to be unified. The adequacy of the treatment will be checked by comparison with the results of mathematical modelling of diffusion in heterogeneous media.[43]

(2) Almost all the structure types described above are represented among specific polymer systems.[44,45] For example, parallel diffusion is observed in polymers with a spherulitic structure when the membrane thickness is comparable with the diameter of the spherulites.[46] Sequential diffusion takes place in lamellar membranes obtained by compressing several films with different diffusion properties, in polymers whose surface has been modified chemically or by radiation, etc. In investigating composites based on polymers and porous specimens the distortions of the diffusion flow lines must be taken into account. The geometrical form of the non-uniformities in the structure must be allowed for in work with crystalline polymers or filled materials.[47]

Diffusion with temporary retention of the diffusant in traps occurs in glassy polymers, block-copolymers, etc. A model for dissociative diffusion will, generally speaking, always be used in describing the processes of mass transport in polymers: the presence of macro-chains necessitates taking into account diffusion along two interconnected channels (along and across the chains) which involve different values of the diffusion coefficient.

The application of the theory of diffusion in heterogeneous media to real polymeric solids often leads to inadequate results: the parameters of the shape of the inclusions calculated from diffusion data do not correspond to those measured on an electron microscope.[21] This is because definite geometrical shapes for the defects in the structure are rarely met in actual systems. Furthermore, a whole spectrum of inhomogeneities in structure is usually present in the materials. Such a situation occurs, in particular, on reversal of the phases.

These difficulties can be overcome by introducing into the modified Maxwell equation a continuous geometrical factor, the values of which are either determined experimentally or calculated by mathematical modelling methods.

(3) In membrane technology a very important aim is to develop methods for a directed choice of the spatial and chemical organisation of the membrane structure, which will ensure that the efficiency and selectivity of the membrane are high. Below we shall set out a theory of diffusion in heterogeneous media for describing the permeability to mixtures of gases and demonstrate a method for choosing a spatial structure of the membrane that is optimal from the point of view of solving problems in membrane-separation of gaseous mixtures.

III. ANALYTICAL TREATMENT OF THE PERMEABILITY OF TWO-COMPONENT HETEROGENEOUS MATERIALS

The following concepts are used in setting up a phenomenological theory of mass-transport in heterogeneous media:

the topology of the medium, i.e. the spatial arrangement of the discontinuities (layers, inclusions, dispersions of inclusions, etc.);

the diffusion properties of the initial components of the medium (the coefficients of diffusion and solubility in these components of the substances being separated);

the type of sorption isotherm of the diffusant in each of the components of the medium; and

the type of diffusion experiment, i.e. a certain set of initial and boundary conditions (in the present work we were restricted to the permeability method).

The output parameters are:

the permeability constant of the heterogeneous medium P which determines the magnitude of the steady-state flow through the membrane;

the mean concentration of the diffusant in the specimen;

the effective non-steady-state diffusion coefficient being used to estimate the time taken to reach a steady state;

the form of the concentration and kinetic dependences;

the dependence of the diffusion parameters on the density of the inclusions and their shape, the structure of the heterogeneous material (thickness and form of the membrane, size of the inclusions, etc.), the partial pressure at the entrance of the membrane, the drop in pressure at the specimen, etc.

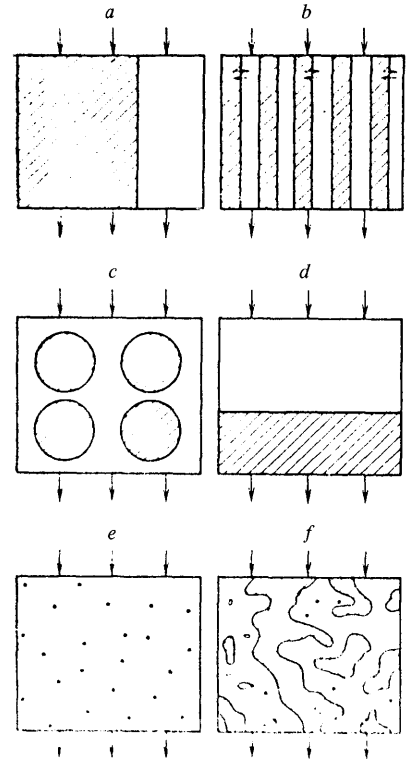


Figure 1. Main types of heterogeneous system.[2]

We are restricted to consideration of five main topological types of two-component material. In the first type of material, mass transport takes place along two channels isolated from each other, i.e. there is parallel diffusion (Fig.1*a*). In the second type of membrane there can be reversible exchange of the diffusant atoms, i.e. dissociative diffusion (Fig.1*b*). In the next type of structure the diffusion medium contains inclusions of a specific shape and size (as an example cubic packing of spheres is shown in Fig.1*c*). A lamellar medium (Fig.1*d*) gives sequential diffusion through layers of different components. The fifth type is a percolation-type structure (a dilute dispersion of point defects is shown in Fig.1*e* and a dispersion of clusters of defects in Fig.1*f*).

The process of diffusion in a heterogeneous medium is usually considered as a random walk of the diffusant particles in the energy field created by the material of the medium (the field does not

change when the diffusant particles pass through it). For a homogeneous isotropic medium the diffusion coefficient D can be represented in the form:

$$D=kd^2$$

with

$$k=k_0\cdot\exp(-\Delta G/k_BT)=\gamma f\nu_0\cdot\exp(-\Delta G/k_BT)$$

where k is the rate constant for the passage of a diffusant atom from one energy state to another, d is the length of a diffusion jump, i.e. the distance between two nearest states, γ is the number of routes by which a transition from one state to another is possible, f is a correlation factor (the fraction of successful jumps, which we shall asume to be 1), ν_0 is the number of jumps in unit time, ΔG is the energy of the transition from one diffusion state to another, k_B is the Boltzmann constant, and T the temperature.

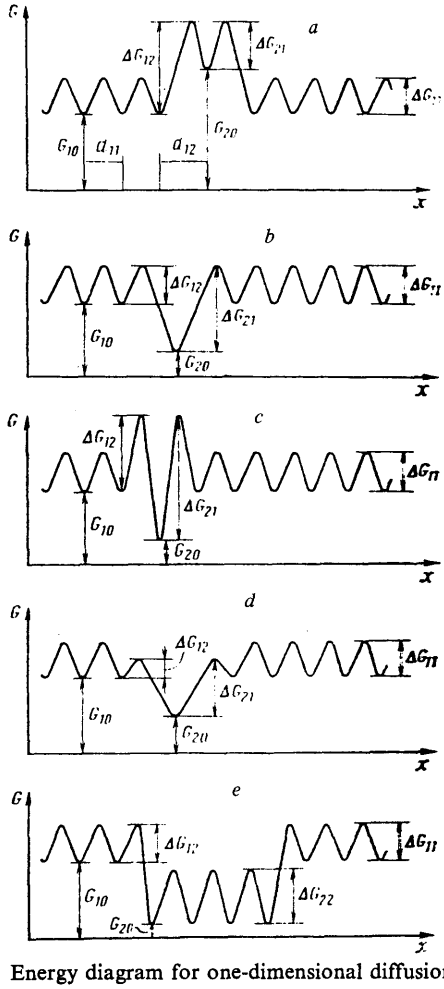


Figure 2. Energy diagram for one-dimensional diffusion (x is distance).[2]

In a two-component medium there are two types of energy state. A site in the base material of the solid will be designated by a subscript 1 and a site in a non-uniformity in the structure by a subscript 2. To describe diffusion in such a system we shall use four transition rate constants k_{11}, k_{12}, k_{21}, and k_{22} and the corresponding lengths of the diffusion jumps d_{11}, d_{12}, d_{21}, and d_{22}. All these parameters are independent of the diffusant concentration but dependent on the temperature:

$$k_{ij}=k_{ij,0}\cdot\exp(-\Delta G_{ij}/k_BT)$$

The pre-exponential factor is determined only by the nature of the diffusant.

Certain types of energy diagram for diffusion in a two-component medium are shown in Fig.2. The migration of the diffusant is determined by the positions of the two potential wells of types 1 and 2 relative to the zero level (i.e. by the energies G_{10} and G_{20}) and also by the magnitude of the energy barriers on entrance to and exit from the potential well (ΔG_{11} for a transition in the base matrix, ΔG_{12} for a transition from the base matrix to an inclusion, ΔG_{22} for diffusion in an inclusion, and ΔG_{21} for exit from an inclusion to the base material of the specimen). If the free energy is higher in state 2 than in state 1 (Fig.2*a*) it is unfavourable for the diffusant to remain in state 2 (an "anti-trap") and it tries to leave. On the other hand, a state with a lower free energy (Fig.2*b*) fills up with diffusant spontaneously (a "trap"). The transition to another phase may be hindered ($\Delta G_{12} > \Delta G_{11}$, Fig.2*c*), remain the same as on transition to an adjacent base state (Fig.2*b*), or may be facilitated (Fig.2*d*), depending on the properties of the boundary between states 1 and 2. If component 2 is an extended inclusion, transitions of type 2−2 appear on the energy diagram (Fig.2*e*).

By the local diffusion coefficient is understood the value $D_{ij} = k_{ij}d_{ij}^2$. Note that $D_{11}\equiv D_1$ and $D_{22}\equiv D_2$ (where D_1 and D_2 are the diffusion coefficients in phases 1 and 2), and that in general D_{12} is not equal to either D_{21} or D_{11}. Thus the presence of additional energy barriers at the entrance to a defect leads to a three-phase diffusion problem for a two-component heterogeneous medium.[48]

By analogy with the concepts used in describing the kinetics of chemical reactions, the value of the ratio of the rate constant for a 1−2 transition to the rate constant for a 2−1 transition is called the equilibrium constant:

$$K=k_{12}/k_{21}=D_{12}/D_{21}=\exp\{-(\Delta G_{12}-\Delta G_{21})/k_BT\}=\exp\{(G_{10}-G_{20})/k_BT\}$$

We shall now turn to a consideration of the population of the energy states of the system by the diffusant atoms. The following symbols will be introduced:

$$\Phi_1=N_1/N=V_1/V,\ \Phi_2=N_2/N=V_2/V\ (\Phi_1+\Phi_2=1)$$

are the volume fractions of components 1 and 2 respectively, where N_1 and N_2 are the numbers of states of types 1 and 2 ($N_1 + N_2 = N$), V_1 and V_2 the volumes of components 1 and 2 ($V_1 + V_2 = V$) in the composite material; the relative populations are $\theta_1 = n_1/N_1$ and $\theta_2 = n_2/N_2$, where n_1 and n_2 are the numbers of diffusant atoms occurring in states 1 and 2; the total population (solubility) of the two-component system is $\theta = n/N = (n_1 + n_2)/(N_1 + N_2)$ and the mean population is $\theta = \Phi_1\theta_1 + \Phi_2\theta_2$.

The linear sorption isotherm is described by the expression:

$$\theta(x=0)=K_\gamma p_0$$

where K_γ is the solubility constant and p_0 the partial pressure of the diffusant on entry to the membrane.

The exchange of the diffusant atoms between the two types of potential well is usually represented in the form:

$$V_1(A)+V_2(0)\underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}}V_1(0)+V_2(A)$$

where V_1(a) and V_2(A) are the diffusant atoms in potential wells of types 1 and 2 respectively and $V_1(0)$ and $V_2(0)$ are vacant sites. If each of the components of the medium is characterised by a linear sorption isotherm then the equilibrium solubility of the diffusant in the first component will be θ_{10} and in the second θ_{20}. Linearity of the sorption isotherm implies that the concentration of free sites in the matrix of the heterogeneous material is sufficiently large, i.e. the relative population is less than 1. At equilibrium:

$$n_2N_1/n_1N_2=k_{12}/k_{21}=K;\ \theta_2=K\theta_1$$

i.e. the equilibrium constant is the ratio of the local solubilities, $K = \theta_2/\theta_1$. Taking into account that the relative population of the first (main) component is not altered by the presence in the material of the second component, the total population is given by the expression

$$\bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2)$$

where θ_{10} is the population of an "ideal" material containing no non-uniformities.

There are various methods for determining experimentally the solubility of the diffusant in the solid: measurement of the mass of the specimen in a steady state of permeability, determination of the amount of diffusant in the specimen after a steady state has been reached, or by dividing the steady-state flow of the diffusant through the membrane by the diffusion coefficient determined from the time lag. In a homogeneous material all these methods give the same result and the solubility measured by the permeability method is equal to half the value determined from the equilibrium sorption. For a heterogeneous medium, on the other hand, such conformity is not observed although the relationship $\theta_2 = K\theta_1$ is always valid.

Let us turn to a consideration of the value of the permeability, i.e. the constant of proportionality between the steady-state flow of the diffusant through the membrane and the difference in the partial pressures on entry to and exit from the membrane. The symbols $\chi_2 = P_2/P_1$ and $\chi = P/P_1$ are used. The known expressions for diffusion in heterogeneous media can now be reduced to a common form of notation.

For dissociative diffusion and its special case of parallel diffusion:

$$\chi=\Phi_1+\chi_2\Phi_2;\ \ \bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2) \qquad (1)$$

For a dispersion of inclusions of identical shape and size (modified Maxwell formula):

$$\chi=(\Phi_1+a\chi_2\Phi_2)/(\Phi_1+a\Phi_2);\ \ \bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2) \qquad (2)$$

where

$$a=a_0/(a_0-1+\chi_2),$$

a_0 being a geometrical factor depending only on the shape of the inclusion. For some simple forms of inclusion this can be calculated analytically: e.g. $a_0 = 3$ for inclusions with a spherical shape and 2 for inclusions in the form of a cylinder with its axis perpendicular to the diffusion flow, etc. Eqn.(2) is valid for dilute suspensions ($\Phi_2 < 0.3$); on changing to closest packing of the inclusions additional terms must be introduced into formula (2).[1] On the whole, Eqn.(2) is satisfied as long as the inclusions retain a definite shape and continuous diffusion flows along one of the components of the heterogeneous medium are possible. It is important to stress that when there is reversal of the phases (i.e. when the matrix and the inclusion change roles) "hysteresis" of the permeability may occur.

For a lamellar material the mean concentration of the diffusant (solubility) in the membrane for a steady state of permeability is given by the expression:[4]

$$\bar{\theta}=\theta_{10}(\chi_2\Phi_1^2+2\Phi_1\Phi_2+K\Phi_2^2)/(\chi_2\Phi_1+\Phi_2)$$

and the permeability is equal to:

$$\chi=(\Phi_1+\Phi_2/\chi_2)^{-1} \qquad (3)$$

The common form of notation for the permeability of the main types of structure which is used in the present work shows clearly the general character of the modified Maxwell formula (2), from which the other diffusion models arise as special cases when an appropriate choice of the geometrical form parameter a_0 ($a_0 \geqslant 1$) is made. The limiting cases are parallel diffusion ($a_0 = \infty$) and sequential diffusion ($a_0 = 1$). This approach allows us to extend the application of the Maxwell formula derived for the case of inclusions of a simple form (discrete integral values of a_0) to cases where the inclusions have an arbitrary structure (continuous fractional values of a_0). Numerical modelling methods can be used to find the values of a_0 for inclusions with the "exotic" shape of rectangular blocks, crosses, etc., for a lamellar medium with a variable boundary, and also to study the evolution of a_0 during reversal of the phases, which results from formation of the nuclei, growth of the nuclei of a new phase, nucleation and growth of the nuclei, etc. The value of a_0 is a measure of the distortions of the flow lines, i.e. the lines along which the product of the diffusion coefficient and the gradient of the diffusant concentration remains constant: for a given χ_2 the smaller is a_0 the greater is the distortion.

In the analysis of the permeability of a dilute dispersion of point inclusions there are considerable difficulties due to the disappearance of diffusion along the second component of the medium at small values of Φ_2. In such structures the transport properties of the material are determined mainly by the characteristics of the inter-component boundaries. In accordance with a statistical treatment,[38] we may write, using our symbols:

$$\chi=\Phi_1^2+\frac{D_{12}+KD_{21}}{D_{11}}\Phi_1\Phi_2+\chi_2\Phi_2^2$$

Using the relation $D_{12} = KD_{21}$, we obtain:

$$\chi=\Phi_1^2+2\frac{D_{12}}{D_{11}}\Phi_1\Phi_2+\chi_2\Phi_2^2 \qquad (4)$$

$$\bar{\theta}=\theta_{10}(\Phi_1+K\Phi_2)$$

The expressions obtained are valid for any values of Φ_2, i.e. they are suitable for describing the permeability of a dispersion of point inclusions during the complete reversal of the phases taking place by a "percolation" process.

IV. MATHEMATICAL MODELLING OF THE PERMEABILITY OF HETEROGENEOUS MEDIA

The analytical approaches to the description of diffusion in heterogeneous media which were discussed previously are valid only with various kinds of assumptions and have a limited use. Numerical methods of mathematical modelling[43] must therefore be used to solve such problems of the permeability of heterogeneous media as transport in a composite containing a concentrated dispersion of inclusions or in a medium containing irregularly shaped inclusions, when there is a complex distribution of non-uniformities through the thickness of the specimen, when there are specific energy barriers at the entry to the inclusion, etc.

In that work[43] modelling was carried out for diffusion in systems with linear sorption isotherms on the basis of the statistical treatment described above. The whole of the heterogeneous material was divided by a rectangular grid into separate cells corresponding to different diffusion states; a matrix of the energy transitions ΔG_{ij} was then set up and from it the rate constants for exchange between diffusion states of different types (k_{ij}) were calculated. After the initial and boundary conditions had been assigned the resultant system of linear differential equations was solved by a Monte Carlo method with a constant time interval.

The program[43] was intended for modelling of mass transport in a two-dimensional heterogeneous medium with an arbitrary topology of inclusions in various diffusion experiments using permeability, sorption, and desorption methods, the method of concentration waves, local diffusion probing, etc. In the course of the calculation the distribution of the concentration of the diffusant in the heterogeneous medium and the total and local flows across the outer boundaries of the specimen are indicated and the total population of the specimen by the diffusant (the solubility) is found. The program also enables a treatment of the kinetic functions to be carried out with the aim of determining the non-steady-state effective diffusion coefficient. For a "percolation" type of medium the program enables a cluster analysis of the inclusions to be carried out, the open, continuous, and closed porosities to be determined, and the mean size of the inclusions to be found.[43] A test of the program, performed for a homogeneous medium, showed a high accuracy ($\sim$0.1%) for the calculation of all the output parameters and also that the postulated functions $k_{ij} = f(\Delta G_{ij})$ are satisfied.

Modelling of diffusion in heterogeneous media was carried out for an extensive set of K, χ_2, and Φ_2 parameters for all the structures discussed above. In the first stage, situations for which analytical formulae are known were investigated and in the second, situations for which there is no phenomenological theory of diffusion.

A test of known published models showed that there is a rigorous mathematical description only for cases of parallel and dissociative diffusion and also for diffusion in a lamellar medium. When extended inclusions of a specific shape and size are present an analytical description is possible for certain simple forms (sphere, cylinder, spheroid), for which the "experimental" values of a_0 agree with the theoretical values and for $\Phi_2 \leqslant 0.3$. As Φ_2 increases the description of the process by the analytical formula becomes worse, with χ approaching χ_2 more rapidly than the theory predicts. We have obtained confirmation [34] of the occurrence of diffusion hysteresis, whereby the permeability of heterogeneous materials of identical composition depends on their method of preparation and in particular on whether a dispersion of component 2 in component 1 was prepared or vice versa. Confirmation was also obtained of the assumption that the geometrical parameter a_0 depends not only on the ratio of the width of the inclusion to its length but also on the "distorting power" of the particular form of inclusion as regards the diffusion flow lines. In particular, the modelling method gave the value $a_0 = 1.55 \pm 0.15$ for an infinite block with a square cross-section placed perpendicular to the direction of flow (the a_0 value for such a geometry cannot be calculated analytically). This value is smaller than the value $a_0 = 2$ for a cylinder because a block with a square cross-section distorts the diffusion flow lines considerably more severely.

It is important to stress that the effect of the geometry of the inclusions on the permeability depends considerably on the energy parameters of the components of the heterogeneous structure. A typical dependence of χ on K and D_2/D_1 is shown in Fig.3; the example shown is of the permeability of a dispersion medium with inclusions in the form of a cylinder, for which $a_0 = 2$ and $\Phi_2 = 0.1$. Thus, when $\chi_2 = 1$ (which does not imply at all that the diffusion properties of the components are identical, since for linear isotherms $\chi_2 = KD_2/D_1$) the permeability is independent of K and D_2/D_1. When $\chi_2 = 0$ (the case of impermeable obstacles) the permeability of the heterogeneous medium depends on both its composition and the geometry:

$$\chi = \Phi_1 \frac{a_0 - 1}{a_0 - \Phi_1} \qquad (5)$$

If, however, the inclusion is highly permeable (a pore, $\chi \to \infty$), the permeability of the heterogeneous medium increases more slowly in the general case, reaching the limiting value $\chi = 1 + a_0\Phi_2/\Phi_1$.

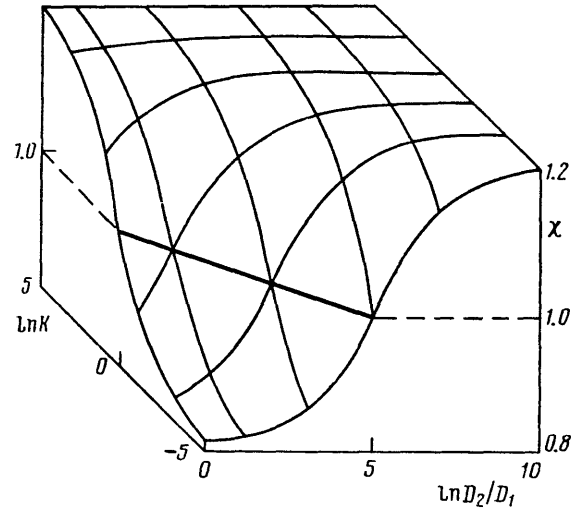


Figure 3. Dependence of the permeability on the transport parameters of a composite[2] (a lattice of cylinders, $a_0 = 2$, $\Phi_2 = 0.1$).

In the modelling of the permeability of a dispersion of point inclusions, the phenomenological model gives only a semiquantitative description. The divergence from theory reaches 20–30% but the theoretical and "experimental" functions $\chi(\Phi_2)$ change in a similar way. The theory is qualitatively correct in prediciting the occurrence of extrema in the function $P(\Phi_2)$ and also their positions, to within $\sim$10%. An attempt was made to improve the accuracy of the numerical calculation by changing the coordination number of the diffusion state from 4 to 8. The discrepancy between the theoretical and "experimental" results was then reached. We assume, although it was not stated when the phenomenological model was set up,[38] that in the statistical summation of the four types of flow it is tacitly understood that the coordination number is equal to infinity. A detailed analysis of this matter showed that, even with high values of the coordination number, complete agreement between the theoretical conclusions and the results of the mathematical experiment cannot be obtained. Thus mathematical modelling of the permeability of heterogeneous media of the "percolation" type by numerical

methods gives more reliable results because in the anlaytical treatments no account is taken of the distortion of the lines of diffusion flow around the point inclusions and their clusters.

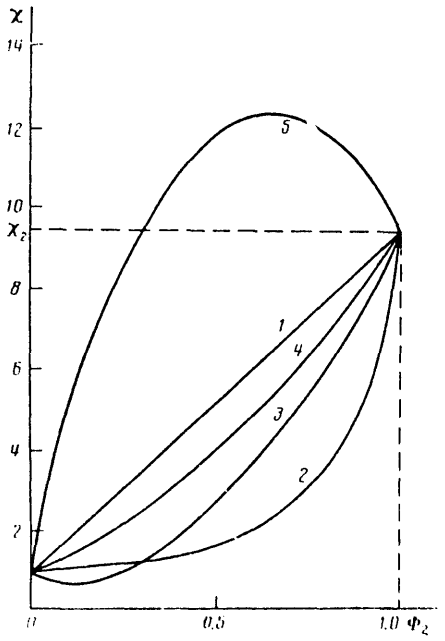


Figure 4. The permeability of percolation-type structures: *1*) parallel diffusion; *2*) a lamellar medium; *3*–*5*) percolation structures for which $D_{12} \to 0$ (*3*), $D_{11} < D_{12} < D_{22}$ (*4*), or $D_{12} \gg D_{11}$ and $D_{12} \gg D_{22}$ (*5*) (from data in Ref.43).

The dependence of the permeability on the volume fraction of the second component is shown for various types of structure in Fig.4. For almost all the structures the $\chi(\Phi_2)$ curves lie between the two limiting cases: dissociative or parallel diffusion (the straight line *1*) and diffusion in a lamellar medium (curve *2*). Exceptions are provided by dispersion structures of the "percolation" type (Fig.1*f*). As follows from Eqn.(4), the dependence of χ on the local transport parameters envisages an effect of the intercomponent layers on the transport (it has already been mentioned that in this case a situation arises which requires the solution of a "three-phase" diffusion problem for a two-component medium). Depending on the conditions at the boundary between the components, the $\chi(\Phi_2)$ curve may pass below the straight line for the limiting case $a_0 = 1$, corresponding to a low permeability of the intercomponent layer ($D_{12} \to 0$, curve *3*), with a possible minimum on the curve; or it may be completely within the permissible region (the permeability of the intercomponent layer lies between the corresponding values for the components of the medium, curve *4*) or it may be situated above the limiting straight line for $a_0 = \infty$. The last situation arises when the permeability is high at the boundary (i.e. when $D_{12} \gg D_{11}$ and $D_{12} \gg D_{22}$, curve *5*), a maximum on the $\chi(\Phi_2)$ curve being possible.

In addition to the steady-state values of the flows, permeability kinetic curves have been obtained by numerical methods[43] and the effective diffusion coefficients calculated.[49] Without discussing these results in detail we note that in a number of cases the theory predicts the possibility that substantial errors will arise in the experimental determination of the steady-state flow of the diffusant through the membrane and hence of the permeability constant. This is because a "pseudo-steady-state" of permeability may be reached for certain values of the local transport parameters; at diffusion times 2–3 times greater than the delay time an almost constant flow through the membrane (significantly smaller than the steady-state flow) is established and this may be erroneously regarded as a true steady state, although times 20–30 times longer are required to achieve the latter.

The total population (solubility) in all the types of structure considered agrees with the values predicted theoretically.

V. SELECTION OF THE STRUCTURE OF THE MATERIAL AS A MEANS OF CONTROLLING THE EFFICIENCY AND SELECTIVITY OF A GAS-SEPARATING MEMBRANE

We have so far discussed the permeability of membranes with respect to any one gas. We shall now turn to the problem of the membrane separation of a mixture of gases and assess the prospects for a directed choice of the structure of the heterogeneous medium in order to achieve the optimum efficiency and selectivity for the membrane.

Suppose that a mixture of two gases is supplied to the input side of a membrane and the process of transport of each of them through the membrane is characterised by its own set of parameters D, K, χ, and θ. These parameters are dependent on the composition and topology of the membrane but independent of the composition of the gaseous mixture. We shall take as the selectivity factor the relationship:

$$\alpha = \alpha_i \chi'/\chi'' \qquad (6)$$

where χ' and χ'' are the permeabilities of the first (object) and second gases respectively and α_i are the selectivity factors of the initial components, $\alpha = P_i'/P_i''$.

The effectiveness of operation of a gas-separating system is characterised by two parameters: the efficiency (i.e. the permeability for the object component, χ'), which determines the amount of product obtained, and the selectivity, which determines its purity. Optimisation of membrane separation is a complex problem because it is far from always possible to obtain high efficiency and a high product purity simultaneously. As is known, membrane separation can be used either to purify the flow passing through the membrane or to concentrate the object product over the membrane. The requirements for selecting χ'' and α are of course different in these cases. If the object product is the gas passing through the membrane, high values of χ' and α are chosen but in the reverse case low values of χ' and α are required.

The effects of the local transport parameters of the heterogeneous medium on the flow of the object component χ' and on the selectivity factor α are different: a decrease in D_2'/D_1' and K' leads to a reduction in χ' and α, but a decrease in D_2''/D_1'' and K'' increases α while leaving χ' unchanged. Since the change in χ' and α in heterogeneous structures of different types takes place differently, then, depending on whether the membrane works by purification or concentration, these parameters will have the optimum values for quite different spatial organisations of the material. It follows from Eqn.(6) that α is a function of six parameters (if the topological factor a_0 is taken as one of them). We shall therefore restrict ourselves to a few examples.

The first two examples are taken from Ref.50 in which measurements were made of the gas permeability of PVTMS (component 1)–PDMS (component 2) block copolymers of various compositions (PVTMS represents polyvinyltrimethylsilane and PDMS polydimethylsilane). We shall discuss Kr–Xe and H_2–Xe gas mixtures, the transport parameters of which are given in the Table (the problem of separating such gas mixtures arises in the AES gas purification system). The Table also shows the experimental values[50] of the steady-state flows and the selectivity factors together with those calculated by us for different structures. For a Kr–Xe mixture the experimental selectivity factor (α = 0.56) is close to the value calculated (0.61) for the parallel (or dissociative) diffusion mechanism (see Table, gas mixture No.1). However, there is a considerable discrepancy between the experimental and calculated values of χ' (2.04 and 10.4 respectively). This may be explained by extra resistance to transport at the boundaries between the components of the block copolymer. In this case the membrane used in the experiment is close to the optimum from the point of view of concentrating the Kr. In using a membrane for Xe purification its efficiency can be increased (by a factor of 5) if a structure which ensures a dissociative or parallel diffusion mechanism is created.

For an H_2–Xe mixture (Table, mixture No.2) the theoretical value of the efficiency with respect to the object material (H_2) is slightly dependent on the structure of the membrane and is close to the experimental value (evidently for hydrogen, resistance to diffusion at the boundary between the components does not play a significant role). However, the theoretical analysis shows that the membrane structure used in the experiment was not the optimum as regards selectivity; in this case a lamellar membrane should be used.

The possible occurrence of extremal relationships between α and the structure are demonstrated on the model example (Table, mixture No.3). Here, to obtain the optimum ratio between the flow and the selectivity a structure having a dispersion of cylinders (filaments elongated perpendicular to the flow) must be created. If, however, it is required to concentrate gas 1 over the membrane and to pass gas 2 through it, then it is better to arrange for sequential diffusion (i.e. to prepare a membrane in the form of layers orientated perpendicular to the flow).

The effect of the structure on the gas-separation parameters χ' and α is conveniently studied using the topology–property diagrams which we have proposed. To construct such diagrams (Fig.5) the reciprocal of the geometrical factor a_0 is plotted along the abscissa (the value of $1/a_0$ varies from 0, corresponding to no perturbation of the flow lines, to 1, corresponding to a severe perturbation) and χ' and α as the ordinate.

Effect of topology and local transport parameters on the permeability (χ') and selectivity (α) of a heterogeneous membrane.*

Mixture no.	Gas	D_2/D_1	K	α_1	Parameter	Calculated for different types of structures**				Experimental (Ref.50)
						I	II	III	IV	
1	Kr	47.9	0.67	1.5	χ'	10.4	1.79	1.41	3.81	2.04
	Xe	160.4	0.52		χ''	25.6	1.82	1.41	8.37	—
					α	0.61	1.46	1.49	0.68	0.56
2	H_2	2.10	1.19	11.0	χ'	1.45	1.30	1.22	1.13	1.4
	Xe	160.4	0.52		χ''	25.62	1.82	1.41	8.37	—
					α	0.62	7.8	9.4	1.5	2.7
3	1	0.1	1.0	7.0	χ'	0.73	0.61	0.27	0.54	—
	2	10.0	5.0		χ''	15.71	1.81	1.42	5.40	—
					α	0.32	2.34	1.33	0.70	—

*The parameters χ', χ'', and α for the gas mixtures nos.1 and 2 were calculated using published experimental data;[50] gas mixture no.3 is a model.

**Φ_2 = 0.3; I) parallel diffusion; II) a dispersion of cylinders; III) a lamellar medium; IV) a dispersion of point inclusions.

These diagrams first of all enable the geometrical factor a_0 to be estimated from gas permeability data. a_0 can be determined experimentally by measuring either the efficiency of the membrane or the selectivity factor. Agreement between the values of a_0 found by different methods indicates the absence of resistance at the boundary between the components. The discrepancy between the values of a_0 obtained from χ' and α (in Fig.5 the range of uncertainty for a_0 is shaded) is large for the Kr–Xe mixture (Fig.5*a*), far larger than the corresponding range for the H_2–Xe mixture (Fig.5*b*).

Such diagrams can thus be used for diffusion-structure analysis, i.e. to determine the topological characteristics of a membrane used in a separation process. On the other hand, they can be used to

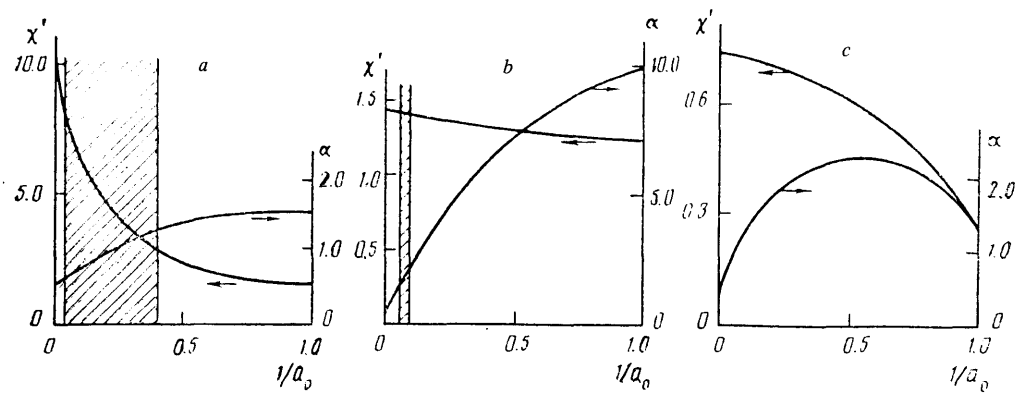


Figure 5. Permeability (or selectivity)–topology diagrams: *a*) separation of a Kr–Xe mixture on a PVTMS–PDMS block copolymer;[50] *b*) separation of an H_2–Xe mixture on a PVTMS–PDMS block copolymer;[50] *c*) a model example (gas mixture no.3 in the Table).[43]

select the optimum structure for gas-separating membranes because, for known transport properties of the initial components, they display clearly the properties of any heterogeneous structures. In the case shown in Fig.5*a* selection of the structure enables primarily the efficiency of the membrane to be controlled, altering it by an order of magnitude; the selectivity, however, is only altered by a factor of 1.5. Fig.5*b* illustrates the reverse case: the structure of the membrane controls mainly the selectivity while the efficiency remains almost constant. A more complex version is shown in Fig.5*c*. Here, as was indicated above, a change in the topology leads to extremal values of α. The region where the extremum occurs is shown clearly in the diagram. Analysis of the component functions χ' and α allows a quick estimate of, for exmaple, the loss in efficiency of the membrane as the selectivity is increased; there is also the possibility of introducing a single component function, the plotting of which requires additional information on a specific chemical-technological process.

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