Translated from *Uspekhi Khimii*, **57**, 876-902 (1988) U.D.C. 541.183.12; 537.311.3; 533.15

From Biological to Synthetic Membranes

S.F.Timashev

The main principles of the functioning of transport systems in biological membranes and especially of processes involving the selective transport of ions and molecules in synthetic membranes (ion-exchange, gas separating, reverse osmosis, ultrafiltration, membranes, etc.) are examined. It is shown that, under the conditions of intense mass and electromass transfer, the transport of ions and molecules in synthetic membranes acquires features characteristic of transport processes in biological membranes both as regards the organisation of the transport (transport via channels) and in terms of the principal kinetic features. The prospects for further research into the physical chemistry of membrane separation processes and processes leading to the formation of new substances, including membrane catalysis, are discussed.
The bibliography includes 115 references.

CONTENTS

I. Introduction 487
II. Characteristic features of ion and molecule transport processes in biological membranes 487
III. The nature of the selective transport of components in synthetic membranes 489
IV. Membrane catalysis 498
V. Conclusions 500

I. INTRODUCTION

Membrane technology is faced by major and large-scale problems whose solution requires the creation of new membrane materials and membranes of different types with effective functional characteristics (permeability, selectivity with respect to the target component, combination of catalytic and separating properties) and also a change-over to intensive mass and electromass transfer conditions in membrane systems (increase in current density, high effective pressure, the use of external influences). This necessitates not only a profound knowledge of the physical chemistry of the membrane separation, the characteristic features of ion and molecule transport processes in synthetic (organic, inorganic) membranes, but also the understanding of the main principles of the functioning of the most effective membrane systems in living nature. The heuristic value of the latter knowledge can be hardly overestimated. In the first place, this is a source of new ideas and concepts concerning the ways of increasing the selectivity of the transport of charged and neutral species, the most effective methods for the intensification of transport processes, the detailed mechanisms of the recording and transfer of information, and the methods for the transformation and utilisation of energy of external sources in a wide variety of processes.

However, in order that these ideas should acquire a pragmatic shape, it is essential to make them available to a wide range of specialists engaged in problems of the physical chemistry of membrane separation and problems concerning the creation of new materials and membranes based on them. This is particularly necessary, since studies on transport processes in native systems and synthetic membranes are prosecuted by different scientific groups almost independently. This article is one of the first attempts at the realisation of this important programme (see also the authors previous communications[1,2]).

II. CHARACTERISTIC FEATURES OF ION AND MOLECULE TRANSPORT PROCESSES IN BIOLOGICAL MEMBRANES

The cells of a living organism include a wide variety of types of membranes and membrane structures[3]—surface membranes (cell or plasmatic membranes) and a multiplicity of intracellular membranes. The surface membranes fulfill important barrier functions maintaining the internal autonomy of the cells and protecting them from the entry of foreign substances. Enzyme transport systems, using the energy stored in the organism and ensuring the supply to the cell and the removal from the latter of different components which makes it possible to maintain the required concentrations of the necessary substances within the cells and in their organelles, function simultaneously in the surface membranes.

Biological membranes consist of lipids and proteins. It has been established that there exist several hundreds of types of membrane lipids. More than half of them (up to 90%) are double layer forming phospho- and glyco-lipids, which manifest pronounced diphilic properties, i.e. they can be divided in space into polar and non-polar parts (the latter consist of hydrocarbon chains).

Under physiological conditions, the double layers are in a liquid crystal state and the description of their molecular organisation must therefore include the dynamic aspect apart from the structural (geometrical) aspect. The lipid double layer is illustrated schematically in Fig.1.[4] An important element of this model comprises the regions in the sublayer *a* in which short-range order ("cluster") is retained, their characteristic transverse dimension amounting to 0.8 nm. They incorporate up to 40–60 hydrocarbon chains (20–30 phospholipid molecules). The molecular packing in the clusters is fairly close to the crystal packing and is "more compact" than in the isotropic region *i* of the double layer.

The clusters are dynamic formations with a lifetime of $\sim 10^{-7}$ s. They are continuously decomposed and reformed, migrating along the double layer. The movement of the lipid fragments in the cluster should then occur simultaneously, i.e. it should represent a cooperative process. The boundary regions between such migrating clusters can be regarded as dynamic defects in the double layer.

In biological membranes, the complex dynamic system of the lipid double layer described includes a large number of protein molecules having different dimensions and shapes. In particular, proteins occupy 35% of the surface of the membrane in erythrocytes. The structural organisation of the phospholipids in the regions corresponding to binding to the protein can then change significantly, so that one may speak of the existence of protein–lipid complexes. The hydrocarbon chains of the phospholipids exist under native

conditions in a quasi-liquid state, the effective viscosity of the double layer amounting to ~5 P at 20 °C and this is why the protein molecules are capable of migrating along the membrane. The "liquid-mosaic" model of the structure of the membranes proposed by Singler and Nicholson has played a major role in the abandonment of the view that lipids constitute a simple structural partition.[3] If one imagines a section through the membrane in the plane perpendicular to its surface, then the proteins incorporated in the membrane double layer must produce a mosaic pattern. Such mosaic model of the membrane, presupposing the existence under native conditions of both double layer sections and regions constituting protein–lipid complexes, is the most attractive.

The distribution of various components (both proteins and lipids) in the membrane is asymmetric for functional reasons. The lateral mobility of the protein fragment in the double layer permits the formation of the most varied structures with a non-uniform (highly non-equilibrium) redistribution of components in the membrane. These can be lipid–lipid and protein–lipid clusters, protein–lipid domains differing in the composition of the proteins and lipids from other regions of the membrane, and domains comprising components within the membrane formed as a result of the binding of the latter to physiologically active compounds distributed on the surface of the membrane. The appearance of such complex metastable formations in biological membranes, which are thermodynamically open systems and exchange matter and energy with the environment, greatly expands the functional possibilities of cell structures.

In order to understand the principal characteristic features of the complex transformations occurring in the transport systems of biological membranes during their functioning, we shall consider the principles of the action of bacterial rhodopsin or bacteriorhodopsin (BR)—the simplest of the transport systems in which photodependent proton transport takes place and a proton electrochemical potential gradient $\Delta\mu_{H^+}$—the macroergy of biological systems according to Metchell's chemo-osmotic hypothesis[5]— is established on the cell membrane. Bacteriorhodopsin is the sole protein component of the purple membranes (PM) ("end-plate") of halobacteria, containing retinal as the chromophoric group, which forms a Schiff base with the protein component of the molecule—opsin BR consists of 248 aminoacid residues.

The attempts to establish the disposition of the protein in the lipid layer were based on the hypothesis that the hydrophobic sections of the polypeptide chain of the molecule should be disposed in the inner hydrocarbon region of the membrane, while the hydrophilic sections should be exposed to the aqueous phase. A scheme for the disposition of BR within the PM in the form of a sequence of seven α-helical blocks passing through the lipid double layer follows from these ideas.[6] The use of computers in order to select the α-helical structures having the lowest energies led to the conclusion[7] that each of the seven α-helical segments contains between 28 and 32 aminoacid residues and that pairs of charged groups form salt bridges within the membrane or are distributed on its surface.

Apart from the absorption in the region of 280 nm, typical for proteins, the BR spectrum is characterised by a broad absorption maximum at a wavelength $\lambda_{max} \simeq 560-570$ nm and a minor band near 400 nm. Continuous illumination of BR with white light shifts λ_{max} in the "light–dark" difference spectrum to the region of 412 nm. The state corresponding to $\lambda_{max} \simeq 412$ nm is stabilised in salt solutions or on lowering the temperature; in the dark, this state relaxes thermally to the initial state. The study of the kinetics of the formation and decomposition of the product absorbing at $\lambda_{max} \simeq 412$ nm by flash photolysis demonstrated the presence of intermediates, which precedes the formation of the product absorbing in the short-wavelength region, and also of a series of subsequent adducts. It has been suggested that the intermediate states be specified in the alphabetical order using the letter subscripts to λ_{max} in the differential optical spectrum.

The schematic photocycle obtained by Lozier et al.[8] is illustrated in Fig.2, which indicates the half-lives of the intermediates at room temperature under physiological conditions. The photochemical process is only the first stage–the formation of the intermediate K which takes place over a period of ~10 ps. This is followed by spontaneous thermally induced transitions between the states, such transitions being increasingly retarded in each succeeding stage. In particular, the activation energy for the K → L transition proved to be 0.5 eV and that for the L → M and M → BR transitions was found to be 0.7 eV. Later measurements[9] in the temperature range from 160 to 300 K yielded 0.68 eV for the activation energy for the

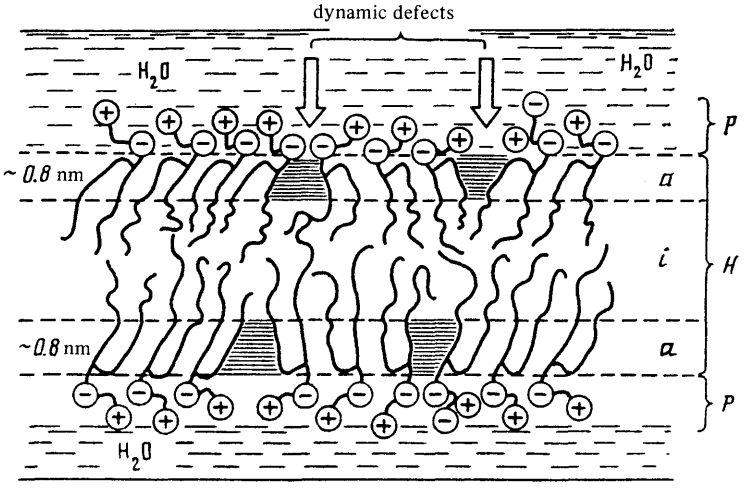


Figure 1. Schematic illustration of the structural organisation of the lipid double layer: *P*–the region of polar groups; *H*–the region of hydrocarbon chains; *a*–"anisotropic" region; *i*–"isotropic" region.[4]

$K \rightarrow L$ and $L \rightarrow M$ transitions. The lower rate of the $L \rightarrow M$ process is caused by the reduced entropy of activation in this stage.

The time of the total turnover of the BR photocycle is 0.01 s under physiological conditions and can increase by several orders of magnitude when the conditions are changed (the temperature and humidity are reduced and certain chemical compounds are present). The O_{640} and N_{530} intermediates cannot always be detected reliably, because the O state is very sensitive to external conditions, for example, to the pH of the medium. The existence of the N intermediate is indicated merely by the presence of the corresponding shoulder on the differential optical spectra. The primary process in the photocycle—the formation of the K_{630} state—takes place under the influence of light even at helium temperatures (2–9 K). A decrease in temperature shifts λ_{max} towards longer wavelengths.

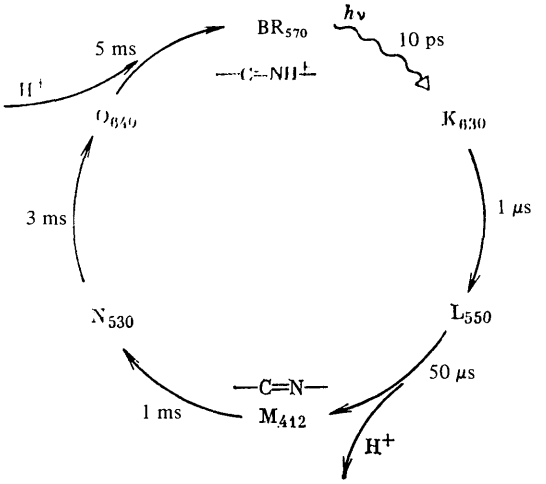


Figure 2. Schematic representation of the photocycle of bacteriorhodopsin[7] (the approximate time of formation of the first intermediate—the batho-intermediate K—and the half-lives of the subsequent intermediates L, M, N, and O are indicated; the subscripts denote the absorption band maxima of the corresponding intermediates in nanometers).

The discussion of the complex processes occurring in this surprising photodependent system and in other transport enzymes is outside the framework of this review (for further details about them, see, for example, Stoeckenius et al.[9]). The corresponding analysis made it possible to formulate appropriately the main principles of the functioning of transport systems in biological membranes.[1,2,10,11]

1. The transport of ions and molecules is determined by the submicrostrucure of the membrane and takes place via submicrochannels—specialised (ionic channels in excited membranes and transport ATPases) or arising in fluctuations of the structure of the lipid double layer. Ion transport with participation of complex forming agents (ionophores) takes place to a limited extent under native conditions.

2. The conductivity of a single ionic channel has multilevel character owing to the possibility of the formation of metastable conformations of the protein subunits of the ionic channels.

3. The selectivity of the ionic channels is determined by the different capacity for hydration of the transported ions and by the presence of regulatory ("gate") polar fragments in the vicinity of the entrances to the channels.

4. The state of the surfaces of the biological membranes (surface enzymes, receptor sections) can determine to a large extent the selectivity of the transmembrane ion transport, the transfer of information within the cell by changing either the charge state or the chemical activity of the surface enzymes as a result of a change in external factors.

5. The transport of ions and water molecules across biological membranes can be achieved under highly non-equilibrium conditions.

6. The transport processes in membranes are highly non-stationary; individual stages of the transport are coupled with conformational transformations in membrane fragments.

7. The ion transport in membranes is influenced decisively by the local electric field within biological membranes. By means of a redistribution of the charge density and by the creation of additional and local electric fields (relative to those already existing), the "mild" utilisation of the energy evolved in the organism in a wide variety of energy dependent processes occurring *in vivo* is achieved, especially in the active ion transport in ATPase (Na^+, K^+-ATPase, Ca^{2+}-dependent ATPase, the H^+-ATPase of the internal membranes of mitochondria) and photodependent (BR) transport enzymes.

8. Ultrahigh temperature thermal fluctuations, occurring in biological systems which are thermodynamically open, have a decisive influence on the characteristics of the activated (including transport) processes in biological membranes and are responsible for the non-Arrhenius character of the activated process.[11,12]

The native systems are immeasurably more complex than the synthetic systems and one can therefore speak merely of a comparison of the most general principles of the functioning of transport systems *in vivo* and of the processes involving the separation of liquid and gaseous mixtures using synthetic membranes in intense mass and electromass transfer. Under intense conditions of membrane separation, the permeability of artificial membranes and the selectivity of the transport through them of different components (ions, molecules) actually depend greatly on the characteristic of the structure, in particular the submicrostructure, of the membrane, of the kind which obtains in biological membranes. The possibility of increasing the efficiency of membrane separation methods actually consists in the specific formation of the structure and state of the surfaces of the membranes in order to impart to them the required properties.

III. THE NATURE OF THE SELECTIVE TRANSPORT OF COMPONENTS IN SYNTHETIC MEMBRANES

The mechanisms of the transport of ions and molecules in synthetic membranes of different types are extremely varied, although they are evidently not as complex as in native membranes. In the analysis of the principal features of ion and molecule transport through synthetic membranes given below we shall concentrate attention on the elucidation of the causes of the selective transport of the components of liquid and gaseous mixtures in polymer membranes which are most widely and effectively employed in membrane technology.

1. Separation of Components in Baromembrane Processes

Reverse osmotic, ultrafiltration, and microfiltration processes are classified as baromembrane processes. The last two processes are evidently determined by the dimensions of the membrane pores or, more precisely, by the pore size distribution function (the characteristic ranges of pore sizes in ultrafiltration and microfiltration membranes are respectively $R_{uf} \simeq 5-50$ nm and $R_{mf} \simeq 0.1-10$ μm). The principal requirements which must be met by such membranes are high thermal and chemical stability (in the first place because of the necessity for periodic regeneration of the membranes by washing in special solutions) and relative uniformity of the pores as regards size when the porosity of the membrane is high.

The characteristic pore sizes in reverse osmosis membranes, $R_{os} \lesssim 1-5$ nm, make it possible to retain the hydrated ions present in solution and at the same time to let through, with a definite degree of selectivity, molecules of different nature (for example, in the separation of mixtures of water with alcohol). A decisive role can then be played not by sieve effects, as in ultrafiltration and microfiltration, but by the influence of the field of surface forces[13,14] (dispersion, Coulombic, and structural forces[15]) on the species (ions and molecules) passing through. The efficiency of the operation of reverse osmosis membranes is therefore determined not only by the pore size distribution but also by the chemical structure of the polymer—the type of functional groups and their mutual disposition in space.

In asymmetric, first-generation, reverse osmosis membranes based on cellulose acetates, the structure of the selective layer (its thickness is usually ~0.2 μm) was not sufficiently rigid. In the course of the functioning of such membranes, some rearrangement of the structure apparently takes place and submicrochannels, which pass through the selective layers and through which a stream of solvent molecules moves (for example, in the demineralisation of salt solutions),[16] are formed.

New generation reverse osmosis membranes permitting the large-scale desalination of natural waters (brackish water, sea water) have been created recently. Composite membranes obtained on microporous polysulphone supports by the interfacial polycondensation of aromatic diamines (for example, *m*-phenylenediamine) with tricarboxylic acid chlorides (for example, trimesic or cyclohexane-1,3,5-tricarboxylic chlorides[17,18]) have the most effective functional parameters. Such aromatic polyamide coatings are characterised by high chemical, mechanical, and thermal stabilities owing to the rigid three-dimensional structure of the polymer molecules resembling the structure of a non-ordered zeolite. High permeability to water (~ 1 m^3 m^{-2} day^{-1}) with a salt retention up to 99.5% at working pressures in the range 20–30 MPa, which are anomalously low for reverse osmosis (on membranes of previous generations such efficiency was achieved at pressures in the range 5.0–6.0 MPa), is then ensured. However, an inadequate stability in relation to sterilising agents, including chlorine, is characteristic of such membranes, which limits the scope of their use for water treatment and for the processing of industrial waste. Increased resistance to oxidants is attained for polymeric materials not containing NH groups, in particular, polypiperazinamides. The corresponding reverse osmosis membranes (developed by the Separam Company) with a selectivity with respect to NaCl of about 95% and an efficiency of ~ 1.0 m^3 m^{-2} day^{-1} (at a working pressure of ~4MPa) are stable in salt solutions at a chlorine concentration of 50 p.p.m.

When water flows during the desalination process through the rigid system of submicropores (cavities) and channels of the selective layer of reverse osmosis membranes, the salt retention is determined both by the size of the channel, connecting the hydrated cavities, and by the random force field generated by all the fragments of the polymer in the region of the channel.

For the calculation of the hydrodynamic resistance of the selective layer, one can use the approaches based on theories of the flow of liquid in a random labyrinth[19,20] which were developed earlier for problems concerning the transport of a non-wetting liquid (for example, mercury) in porous materials.[21,22] According to Neimark,[22] it is useful to represent the pore distribution in space in the form of a three-dimensional lattice whose linkages (edges) correspond to the pore channels and the nodes correspond to the sites of their intersection, i.e. the cavities. In this approach, the problem of the relative distribution of the liquid and gaseous phases (the cavities and channels which are respectively filled and unfilled by water molecules) reduces to the classical problem of the theory of flow—the problem of percolation via connections.[19]

We shall consider the process involving the "forcing" of a non-wetting liquid into a pore system.[22] At an excess pressure P, the non-wetting liquid can be forced through pore channels whose effective size exceeds a certain quantity R_+, which depends on P and the field of surface forces in the channel. Such pore channels with $R > R_+$ will be called supercritical. The fraction p of supercritical pore channels is determined by the channel size distribution function $\varphi(R)$:

$$p = \int_{R_+}^{R_{max}} \varphi(R)\, dR.$$

Considering the liquid phase in terms of the macroscopic approximation, it is convenient to introduce the concept of the surface tension (coefficient) σ_s at the liquid–vapour interface and of the wetting angle θ. For a cylindrical pore, $R = 2\sigma_s \cos\theta/P$.

At an excess pressure P, the non-wetting liquid penetrates only into the pores which are linked to the outer surface of the specimen by a sequence of supercritical pore channels. It is known that for $p < p_c$, where p_c is the lattice percolation threshold, the probability of the existence of a continous sequence of supercritical channels decreases exponentially with increase in the length of such sequence. Under these conditions, the non-wetting liquid penetrates only into supercritical pores in the immediate vicinity of the outer surface. Only when the excess pressure increases so much that the fraction p of the supercritical pore channels exceeds the percolation threshold p_c does the non-wetting liquid penetrate into the bulk of the specimen. The corresponding pressure is referred to as the break-through pressure. Its value p_c is determined from the relation

$$p_c = \int_{R_+(P_c)}^{R_{max}} \varphi(R)\, dR. \qquad (1)$$

The phenomenon of break-through (the penetration of a non-wetting liquid into the bulk of the specimen) at $p > p_c$ is due to the formation of an infinite connected system of supercritical pores or of an infinite cluster (IC). The IC incorporates cavities (nodes) and supercritical channels (edges or connections) and the cavities are connected to the outer surface by a continuous sequence of supercritical channels. For large specimens containing a macroscopically large number of elementary pores, one can neglect the edge effects and assume that the IC is distributed uniformly in the bulk of the specimen and that the degree of saturation (it characterises the relative volume of the liquid phase in the overall volume of the system of pores and channels) of a specimen having finite dimensions is equal to the corresponding quantity for a semi-infinite medium.

We shall assume that the pore channels of different sizes are distributed at random. Then the distribution of the supercritical channels in the lattice will also be random: the probability that an arbitrarily selected connection is supercritical is equal to the fraction p of the supercritical pore channels. The following characteristics of the IC are considered in the percolation theory: the connectivity function $Q_c(p)$—the fraction of connections included in the infinite cluster among all the lattice connections; the percolation probability $Q_p(p)$—the fraction of nodes included in the IC relative to all the lattice nodes; the relative conductivity $\sigma(p)$—the ratio of the lattice conductivity, in which conductors constitute a fraction p and the fraction of insulators is $1 - p$, to the conductivity of the lattice in which all the connections are conductors. The characteristics of the relative phase distribution are expressed in terms of these functions. In the example considered, the non-wetting liquid occupies the pores incorporated in the IC formed by supercritical connections and the degree of saturation λ is expressed in terms of the connectivity function and the percolation probability:

$$\lambda = v_p Q_p(p) + (1 - v_p) Q_c(p), \tag{2}$$

where v_p is the fraction of the volume of the cavities in the overall pore volume and $1 - v_p$ the fraction of the volume of the pore channels.

The effective transport coefficients of the liquid in the system of channels are porportional to the conductivity of the IC:

$$D(\lambda) = D(1)\sigma(p), \tag{3}$$

where $D(\lambda)$ and $D(1)$ are the effective transport coefficients for a degree of saturation λ and for the complete filling of the pore space respectively.

The connectivity function, the percolation probability, and the relative conductivity for a simple cubic lattice have a non-linear threshold character and are identically equal to zero for $p < p_c$. Such behaviour is typical for any lattices regardless of their topology. The percolation threshold is mainly determined by the lattice coordination number z. The approximate equality $p_c \simeq 1.5/z$ is known to hold. In the vicinity of the percolation threshold, the asymptotic scaling relations are valid:

$$Q_p \propto Q_c \propto (p - p_c)^{\beta}, \tag{4}$$

$$\sigma \propto (p - p_c)^{t}. \tag{5}$$

The critical indices of the percolation probability (β) and conductivity (t) are[22] in the ranges $0.35 < \beta < 0.47$ and $1.5 < t < 2.0$. Under conditions remote from the percolation threshold, the linear equation of the self-consistent field theory is valid for conductivity $\sigma(p)$:

$$\sigma(p) = \left(p - \frac{2}{z}\right)\left(1 - \frac{2}{z}\right)^{-1}. \tag{6}$$

The percolation probability $Q_p(p)$ and the connectivity function $Q_c(p)$ can be fitted[23] by a power relation; at $p \gtrsim 2p_c$, they differ little from the asymptotic relations:

$$Q_p(p) \to 1, \quad Q_c(p) \to p. \tag{7}$$

According to the scaling hypothesis, the geometry of the percolation system, including the structure of the IC, is determined by a single characteristic dimension—the correlation length L. Under conditions remote from the percolation threshold at $(p - p_c)/p_c \simeq 1$, the correlation length can be of the same order of magnitude as the size $\overline{R}_1$ of a single structural element. At $p \to p_c$, the correlation length increases without liimit in accordance with the power law

$$L \propto (p - p_c)^{-1+\delta}. \tag{8}$$

The critical index of the correlation length for three-dimensional lattices is $1 - \delta \simeq 0.9$.[22] For distances $r \gg L$, the IC is homogeneous and for $r \ll L$ a correlation in the distribution of elements belonging to the IC is manifested. In the vicinity of the percolation threshold, where $L \gg \overline{R}_1$, there is a region where $\overline{R}_1 \ll r \ll L$, in which the IC possesses the so called fractal properties, i.e. it is characterised by a non-traditional dependence of its volume (or surface) on the geometrical scale. For example, the number of elements in the IC at a distance $r' < r$ from a selected element increases in proportion to r^{d_f}, where the so-called fractal dimensionality d_f is not equal to the dimensionality of the space d:

$$d_f = d - \beta/(1 - \delta) \tag{9}$$

(in the three-dimensional case, $d_f = 2.5$). Ideas concerning fractal properties of the IC proved fruitful in the study of the geometrical features of the relative distribution of phases in the pore space.

The dependence of the relative conductivity σ on the fraction of the elements incorporated in the IC is of interest for the calculation of the effective transport coefficients in partly saturated porous media. It follows from the scaling relations (4) and (5) that

$$\sigma \propto Q_p^{t/\beta} \propto Q_c^{t/\beta}. \tag{10}$$

From Eqn.(2), it follows that in the scaling region the effective transport coefficients with respect to the non-wetting phase are linked by a power relation to the degree of saturation and that the power exponent is equal to the ratio of the critical indices of the relative conductivity and the percolation probability:

$$D(\lambda) \propto \lambda^{t/\beta}. \tag{11}$$

An interpolation expression for $D(\lambda)$ has also been obtained:[22]

$$D(\lambda) = D(1)\frac{2.88}{(1 + 1.31 v_p)^{3.48}}\lambda^{3.48} \quad \text{for } \lambda < 0.433(1 + 1.31 v_p). \tag{12}$$

The characteristic features of the penetration of a non-wetting liquid into porous systems can be analysed on the basis of Eqns.(11) and (12) as a function of the applied pressure. However, for the corresponding analysis of the permeability to water of reverse osmosis membranes it is essential to possess independent data on the structural parameters of the selective layer, including the pore size distribution function and the surface force field parameters. Unfortunately, there are virtually no such data at the present time. When the appropriate investigations are carried out, it will become possible to assess more effectively the potential possibilities of the method of reverse osmosis for the separation of various, including aqueous organic and organic, liquid mixtures. At the present time relations of type (11) and (12) have been established for gas and electrolyte transport processes in porous nickel electrodes.[24]

Ultrathin surface layers of submicroscopic thickness (~ 10 nm), made of organic and inorganic (for example, polyphosphazenes) materials and produced on ultrafiltration or microfiltration supports, can serve as carrier structures with fractal properties in the separation of mixtures of electrolytes, in the separation of gaseous mixturres under intense separation conditions, and in electrocatalytic processes. Not only the corresponding permeability constants but also the parameters of the selectivity of the separation can then depend on the thickness of the ultrathin layer. The ways of creating such structures can be related to the use of the Langmuir—Blodgett method for the formation of monomolecular films and mixed structures with a high degree of molecular order and of the electrochemical, plasmachemical, and photochemical methods for the deposition of ultrathin layers. In fact one is dealing with a qualitatively new level of membrane technology, because the permeability

of the membranes to the target components increases by more than an order of magnitude and hence there is a significant decrease in the materials consumption in the membrane process. The technical sophistication involved in the creation of such barrier structures and ultrathin layers must be the highest possible and must involve an ultrapure technology (as regards materials and the concentration of aerosols in the surrounding space) employing the experience and methods of electronic industry.

2. The Diffusion-Migration Transport of Species in Membranes

In many synthetic membranes, molecules and ions are transported via a mechanism involving the dissolution of the components in the membrane matrix and the subsequent diffusional or diffusional-drift transport through the bulk of the membrane. In membranes of this type (ion-exchange and gas separation membranes) there are no rigidly fixed pores, although they do possess a definite free volume. In the case of flexible chain polymers, the effects associated with the redistribution of the free volume due to the mobility of fragments of the matrix play a decisive role in transport processes.[25] In rigid chain polymers (below the glass point T_g), the efficiency of the transmembrane transport of species is usually correlated with the structural non-equilibrium nature of the polymer matrix, characterised by the presence of definite submicrocavities in the vicinity of bulky substituents in the side chains.[26–28]

The traditional method of describing mass and electromass transfer processes in non-porous membranes involves the use of quasi-equilibrium ideas and the neglect of the "surface resistance", it being supposed that the transport of ions and molecules through the boundary regions takes place at a high rate (at the membrane–medium interfaces, there is equilibrium with respect to the species which have crossed the membrane). Therefore, if the membrane separates two volumes of gas with different concentrations of species of one kind, then, together with the consideration of local values of the diffusional flux of species in the membrane

$$J = -D\frac{\partial c}{\partial x} \quad , \tag{13}$$

where $c(x, t)$ is the local concentration of species in the membrane, D the diffusion coefficient, x the coordinate normal to the surface of the membrane, and t the time, it is necessary to introduce the sorption isotherm of the component in order to determine the concentrations of species near the surface. On the simplest assumptions concerning the form of the isotherm (the Henry isotherm), an expression follows from Eqn.(13) for a stationary flux of species passing through the membrane:

$$J = \Pi\Delta P/d;\ \Pi = D\gamma \quad , \tag{14}$$

where Π is the permeability constant of the material, γ the thermodynamic parameter of the solubility of the component in the given material (the Henry constant), ΔP the drop of the pressure of the component across the membrane, and d the thickness of the membrane. If the species migrating in the bulk of the membrane is acted upon by lateral forces—in the presence of an electrical potential gradient $\partial\varphi/\partial x$ (transport of particles with an electrical charge q) and also in the presence of a convective flux (for example in the case of transport in liquid and quasi-liquid membranes)—then the expression for the local flux of species J assumes the form

$$J = -D\frac{\partial c}{\partial x} - c(x)\cdot\left[\mu\frac{\partial\varphi}{\partial x} - u\right] \quad , \tag{15}$$

where μ is the electrical mobility of the species linked to the coefficient D by the Einstein relation $\mu = \xi qD/k_BT$ (T is the absolute temperature, k_B the Boltzmann constant, and $\xi \simeq 1$ a phenomenological numerical parameter) and u is the rate of drift of the species under the influence of the convective movement of the medium. The use of Eqn.(15) together with the sorption isotherm of the component transported in the membrane makes it possible to generalise Eqn.(14) and to take into account simultaneously the diffusion, electrodiffusion, and convective diffusion processes.

In considering the diffusional transport processes in real solid-phase membranes, inorganic and polymeric organic, complications arise due to the presence in them of different kinds of inhomogeneities: structural defects and inclusions of another phase. These defects and inhomogeneities can serve as capture sites for the given species, can give rise to local mechanical stresses influencing the transport processes, can effectively sort the diffusing components, etc. The description of mass transfer in such inhomogeneous media is complex even under the conditions of small fluxes of the transported species. The situation becomes immeasurably more complex if it is necessary to take into account non-linear effects associated, for example, with the characteristics of the sorption of the diffusing components in an inhomogeneous matrix.[29] Intuitively it is clear that the description of the transport of species must be based on the use (appropriately justified) of effective diffusion coefficients D_{eff}, which depend on the characteristic features of the transport of the species in those regions of the membrane which are characterised by different equilibrium solubilities of individual components and also on the spatial distribution of such regions in the matrix.[30]

3. Non-Equilibrium Transport Conditions

The traditional quasi-equilibrium approach to the description of processes involving the membrane separation of the components of gaseous and liquid mixtures is justified only for a low density of the fluxes J_i of the components i crossing the membrane, when $J_i \ll J_{io}$, J_{io} being the "exchange flux" density of the component i in the regions of the membrane–external medium interfaces and also at the boundaries between the micro- and submicro-regions in the bulk of the membrane differing in structure. In such cases there is equilibrium with respect to the species i in different regions of the system and the fraction of the species passing to each of the structurally different regions within the membrane is determined by the thermodynamic parameters of these regions.

On passing to extremely highly non-equilibrium regimes in membrane separation under the conditions of electrodialysis, electrolysis, and elevated pressures in gas separation, when $J_i \lesssim J_{io}$, the quasi-equilibrium models of the "dissolution and diffusional-migration transport" become inadequate. Under these conditions, the state of the membrane–medium interface determines the character of the distribtuion of the transported species between the external medium and the membrane. The state of the boundary separating regions with different physicochemical characteristics in the bulk of the membrane determines the distribution of the pathways (fluxes) of the species in the membrane matrix and, with increase in J_i, the condition $J_i \simeq J_{io}$ begins to hold at a greater number of interfaces. It therefore becomes necessary to consider in previously structurally indistinguishable regions increasingly finer details (with dimensions down to several nm), which influence the redistribution of the species in the matrix under the conditions of intense mass transfer. The transport of molecules and ions through synthetic membranes

acquire certain features characteristic of the most effective membranes—namely biological membranes, both as regards the type of organisation of the transport (transport via "channels") and as regards the principal kinetic relations.

We shall consider below a series of problems in the model description of transport processes in membrane systems under extreme regimes and shall demonstrate what new possibilities can arise in the membrane separation of liquid and gaseous mixtures under these conditions.

The transition from quasi-equilibrium mass transfer regimes to extreme (non-equilibrium) regimes can be conveniently illustrated in relation to the transport of the molecules of simple gases through membranes based on siloxane–containing block copolymers. A relation between Π and ΔP has been observed[32,33] in a study of the permeability of such membranes to the molecules of simple gases (CO_2, O_2, and N_2), which consists in a considerable (severalfold) increase in Π when P changes from 1 to 5 kPa. According to quasi-equilibrium ideas, Π = const if D and γ are independent of pressure. In an analysis[34] of the sorption isotherms of the molecules of simple gases (CO_2 and O_2) in siloxane-containing Silar block copolymers, no anomalies were noted: the adsorption isotherms were linear throughout the experimental pressure range (up to 75 kPa). It is therefore most natural to assume that, under conditions[32,33] where $P > 5$ kPa, the filling of both phases of the block copolymer, rigid and flexible, is non-equilibrium and transport takes place mainly in the flexible phase. The latter conclusion is also confirmed by the results of a study[35] in which correlations were observed between the mobility of the fragments of the siloxane phase of the block copolymer and the effective diffusion coefficients.

On passing to non-equilibrium mass transfer regimes, the effective solubility parameter σ differs from the equilibrium value γ ($\sigma < \gamma$), which leads to the possibility, in principle, of influencing the permeability constants of membranes by modifying the membrane–medium interface. This possibility has been realised in a study[36] where it was shown that the chemical modification of the gas–polymer interface by the polymerisable fluorine-containing allyloxysilane, which exhibits surface-active properties, can increase almost by a factor of two the permeability constants Π of the modified membranes relative to the corresponding values for the initial (unmodified) membranes. Under the conditions of such modification, the diffusion coefficients D of gases in the membranes remain almost unchanged and DSC [differential scanning calorimetry?] data also indicate the unchanged state in the bulk of the membrane after its modification: the thermograms of the initial and modified membrane are completely identical. The equilibrium value γ should not therefore change as a result of the above modification and the observed effect must be attributed to a change in the effective solubility: $\sigma_{mod}/\sigma_{init} \simeq 2$.

In order to solve the problems of membrane separation in non-equilbrium transport regimes, another procedure is needed, in particular the use of the method of the theory of flow (of a liquid in a random labyrinth).[19–20] Here the effective pathways in the transmembrane transport of species ("infinite clusters"—IC, in terms of the terminology of the theory of flow) are produced by a system of localisation centres separated from one another by an optimum average distance. This situation obtains in the transport of ions through perfluorinated sulphonic acid cation-exchange membranes characterised by a specific submicrostructure characteristic of comb polymers: the hydrophobic matrix at the hydrated ionogenic group in the amorphous regions of the perfluorinated polymer forms associated species—"clusters" with characteristic dimensions of ~5 nm.

A fragment of the amorphous part of the perfluorinated sulphonic acid cation-exchange material is illustrated in Fig.3. According to this structural model, the pathways followed in the flow of ions and water molecules are within ion-exchange clusters ("ionic channels" in a hydrophobic matrix). The transport of ions over macroscopic distances (the formation of IC) becomes possible for a sufficiently high degree of hydration of the ionogenic groups (centres between which ion jumps are effected), whereupon an effective linkage is established between adjacent ionogenic groups.

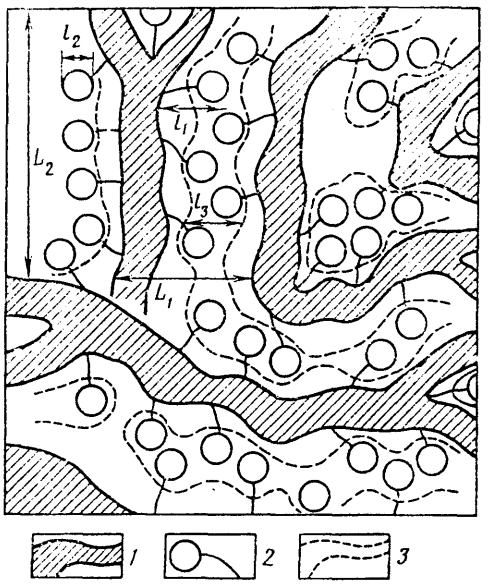


Figure 3. Schematic illustration of a fragment of the amorphous part of a sulphonic acid cation-exchange membrane:[37] 1) main polymer chain; 2) hydrated counterions and ionogenic groups under the conditions of a low moisture content (the "chlorine electrolysis" conditions); 3) "channels" for the transport of ions and water molecules in the presence of a high moisture content; the distance $L_1 \simeq$ 4 nm is estimated from low-angle X-ray scattering data, $L_2 \simeq$ 10 nm from Mössbauer spectroscopic data, l_1 and l_2 from DENR and NMR data, and l_3 from data obtained by reference porometry and DENR.

Under the conditions of a high moisture content when the average number of water molecules n per ionogenic group exceeds 15, virtually all the functional groups of the membrane are "bound" and the polymer matrix is on average uniformly threaded by a random network of channels hydrated to the maximum extent, through which the diffusional transport of ions takes place. The specificity of such ionic transport is low.

With decrease in the moisture content, some of the "bonds" between adjacent centres are broken so that "dead ends" appear in the random network of channels.[20] In the flow model, the dependence of the specific resistance of the membrane ρ on the moisture

content for low values of n ($n < 10$, "chlorine electrolysis" conditions) is of the form[37]

$$\rho \simeq \frac{R_0 r_c}{[\nu(n) - \nu_c]^{2-\delta}} \cdot \exp\left[p\,(\bar{n}^{1/s} - n^{1/s})^{\mu_s} + \frac{\varepsilon(n)}{k_B T}\right], \qquad (16)$$

$$p = \left[2\alpha_s \left(\frac{3}{4\pi\rho_0}\right)^{1/s}\right]^{\mu_s}, \quad \bar{n} = \frac{1}{6}\pi\rho_0 r_c^3,$$

where R_0, α_s, and μ_s are parameters determining the probability of the jump by ions between adjacent ionogenic groups, $\varepsilon(n)$ is the activation energy for such a jump, $\nu(n)$ the average number of bonds between a specified ionogenic group and adjacent groups whose centres are separated from the centre of the specified group by distances not exceeding the characteristic average value r_c, ν_c is the threshold value of $\nu(n_c)$ for which IC arise, and ρ_0 is the effective density (packing density) of water molecules in the hydrated ionogenic group–counterion complex.

Attention should be drawn to the decisive role of the entropy factor in Eqn.(16) which depends exponentially on n and is determined by the parameters α_s, μ_s, and r_c in establishing the specificity of the ionic transport. A similar situation apparently arises also in the ionic transport in biological membranes. In the region of low values of n, the following relations between the quantities ρ for ions of different types (for a fixed n) are valid in the case of sulphonic acid cation-exchange membranes:

$$\rho_{H^+} < \rho_{Li^+} < \rho_{Na^+} < \rho_{K^+} < \rho_{Cs^+}.$$

Analysis of the relation obtained permits the conclusion that there is contact interaction of the hydrated cation with the ionogenic centre (the sulpho-group), which is consistent with Eisenman's series XI in the binding of ions within the channels of membranes capable of being excited.[38] This means that the ionic channels of sulphonic acid cation-exchange membranes are systems with a high "field strength" (such as, for example, the Na^+-channels in the squid axon). The creation of membranes with other types of ionogenic groups ensures new possibilities for the selective transport of ions and leads to the realisation of other Eisenman selectivity series (for example, among the eleven which exist for cations).

Spectroscopic studies using ^1H and ^7Li NMR[19] have shown that the character of the relation defined by Eqn.(16) is determined by the characteristics of the elementary ion transport between the functional groups. This means that the specificity of ion jumps under the conditions of limited capacity for hydration of the functional groups (this situation actually obtains also in the ionic channels of biological membranes) is associated with the entropic multipliers of the rate constants for the corresponding jumps. For ions of different types, one may point to certain critical values of n_i such that, for $n < n_i$, the transport of ions of type i is significantly retarded as a consequence of the formation of cation–functional group contact ion pairs. When sulphonic acid cation-exchange membranes are used, these values for the H^+, Li^+, and Na^+ ions are respectively ~ 2, ~ 4, and ~ 6. In particular, this is indicated by the dependence of the chemical shift of the water protons in the membrane on the moisture content of the latter:[39] for $n > n_i$, the ions indicated retain their individuality in the membrane—they exist in the form of the complexes $[H_5O_2]^+$, $Li^+.4H_2O$, and $Na^+.6H_2O$.

One of the main consequences of Eqn.(16) is large local heat evolution in perfluorinated membranes when a high-density electric current j passes through them (under the conditions of "chlorine electrolysis" and $j \simeq 0.3$ A cm^{-2} and when the overall moisture content in the membranes is low, we have $\nu \gtrsim \nu_c$ because of the high concentration of the resulting alkali, reaching 20–40%). It has been shown [20] that, in the vicinity of the flow threshold, the bulk of the Joule heat is evolved within a small volume on a limited number of "bonds" (at the "heating points")[40] and in the limit $\nu \to \nu_c$ the fraction of the volume carrying almost the entire Joule heat tends to zero.

Before discussing certain consequences arising from the above, we may note that perfluorinated ion-exchange membranes are "non-cross-linked". Therefore, under the influence of local heat evolutions, the conformation of the polymer chains in the membranes may change, giving rise to the formation of metastable structurally-conformational states of the amorphous fragments with an arrangement of the side chains characteristic of each such state.

For sufficiently extreme electromass-transfer regimes under the conditions of a low moisture content in the region of the "heating point", there is a possibility of a virtually complete dehydration of the functional groups, so that the probability of ion jumps in this region falls sharply and the corresponding transport section is eliminated from the IC. However, the "evaporated" water molecules formed on dehydration can hydrate functional groups which had not been previously included in the IC and a new percolation pathway arises. The above mechanism of the "flickering of transport pathways" ensures high thermal stability of the non-cross-linked perfluorinated ion-exchange materials.[37]

One may note that the effective mechanical properties of the non-cross-linked copolymers, necessary for the functioning of the membrane in such extreme regimes, are determined by the PTFE crystallites ensuring the "physical" reinforcement of the perfluorinated matrix. Such crystallites (their characteristic size is ~ 10 nm) are formed by fragments of different copolymer molecules without functional groups. The intermolecular distances realised in PTFE crystallites at room temperature are attained in PTFE crystals at elevated temperatures (470–490 K). Closer packing of the above fragments is prevented by the presence of functional groups in the macromolecules. In order to diminish the "wedging" influence of the ionogenic groups on the PTFE crystallites, perfluorinated membranes are obtained from ternary copolymers [in particular, in polymerisation one introduces, apart from tetrafluoroethylene and the perfluorinated ester with sulphonyl fluoride or carbonyl fluoride groups, a third monomer of the type $CF_2 = CFO(CF_2)_3CF_2$, which is responsible for the formation of buffer zones between the PTFE crystallites and the amorphous section containing ionogenic groups; this improves the mechanical properties of the membranes].

4. Characteristics of the Transport of Species in Liquid and Quasi-liquid Membranes

A promising development is the use of liquid and quasi-liquid† membranes for the selective extraction of target components. It has been suggested that they be used[41,42] especially for the extraction of metals in hydrometallurgical industries, for the concentration of valuable components in waste and natural waters (including sea water). In this connection, a series of problems arise: (1) the development of a scientific basis for the search for complex-forming

†Quasi-liquid membranes or impregnated liquid membranes are understood to constitute liquid systems (the solvent with the complex-forming agent, catalyst, etc. contained in it) immobilised in an inert porous base; in the foreign literature the term "supported liquid membranes" is usually employed for such membranes.

agents ensuring a high extraction selectivity; (2) stabilisation of complex emulsions ("Li membranes"[43]) and film systems (in Boyadzhiev's columns) for the solution of technological problems in liquid membrane extraction; (3) enhancement of mass exchange processes in the region of the liquid membrane–liquid medium interfaces.

We shall confine ourselves to considering only mass exchange processes without dwelling on problems of the description of transport in the region of membrane–medium interfaces in view of the necessity to use boundary conditions of a fairly general type.[16]

As shown previously by Lev and Buzhinskii,[45] the formation of complexes in the interfacial region by the transported species with complex-forming agents present in the liquid membrane may retard the process and lead to the appearance of "surface" resistance. However, the situation can become still more complex when such complex formation occurs in macroscopic (~ 1 μm) regions of liquid membranes, for example, as a consequence of the formation in such layers of submicrodispersions of the external (in relation to the membrane) solution. In this field, there are still many fundamental difficulties to be overcome.

We shall consider the problems of mass transfer associated with its enhancement by spontaneous convection, which may develop in the boundary regions of the liquid membrane (and the electrolyte if it constitutes a medium external in relation to the membrane).[46] We shall confine ourselves to considering the classical problem of the transport of CO_2 molecules through liquid and quasi-liquid membranes formed on the basis of aquous alkali metal carbonate solutions, in connection with the results obtained recently,[47] which demonstrated the fundamental role of the effects of the spontaneous convection of the solution in this process.

The mechanism of the transport of CO_2 through liquid alkali metal carbonate layers can be represented in a simplified way by the following two stages:[48]

(1) dissolution of carbon dioxide accompanied by a heat change of ~ 26.2 kJ mol^{-1}:

$$CO_2 + CO_3^{2-} + H_2O \rightarrow 2HCO_3^- ;$$

(2) the transport of HCO_3^- ions through the membrane and the evolution of carbon dioxide on the other side of the membrane where the CO_2 partial pressure is reduced and the reverse reaction

$$2HCO_3^- \rightarrow H_2O + CO_3^{2-} + CO_2$$

takes place. The process is accelerated when catalysts are introduced into the system, such catalysts frequently consisting of the anions of weak acids, for example, arsenic acid.

The kinetics of the transport of CO_2 through a liquid membrane consisting of a layer of liquid (3.2 *N* Cs_2CO_3 + 0.25 N Na_3AsO_3 solution; pH 13.6) enclosed between two hydrophobic asymmetric polyvinyltrimethylsilane films have been investigated.[47] These films exhibit a high gas permeability (the permeability to CO_2 is 3×10^{-8} mol m^{-1} s^{-1} Pa^{-1}), so that they do not introduce any distortions into the measurements (error $\leqslant 0.5\%$). The kinetics of the transport of carbon dioxide were investigated for the horizontal and vertical positions of the cell. For the horizontal position of the membrane, CO_2 was supplied to the cell in two ways: in one case carbon dioxide was injected into the upper cavity and a carrier gas (helium) into the lower cavity, while in the second case the opposite arrangement was used. As a result, the coefficients of the gas permeability Π of membranes of different thickness d were found at +20 °C.

It was noted[47] that, for the horizontal position of the cell, a steady increase in Π with increasing d was observed. The permeability coefficients depended on the way in which gas was supplied into the cell, the difference between the values of Π increasing with decrease in the thickness of the membrane. For the vertical position of the cell, Π initially increased with increase in d and then fell sharply. The values of Π for different orientations of the membrane differ by more than an order of magnitude (for $d = 3600$ μm).[47] Such behaviour of Π can be explained only by convective movements in the solution.

The appearance of convective movements within the liquid membrane can be caused by different factors. In particular, the heat evolution of dissolution of CO_2 induces local heating in the membrane and hence changes in the surface tension at the gas–liquid interface leading to Marangoni effects. It is therefore of interest to calculate formally the diffusion coefficient D and the solubility σ_{eff} of CO_2 molecules in the carbonate solutions on the basis of the model of the transmembrane gas transport, which includes the instantaneous dissolution and diffusional transport as the limiting stage. According to this model, $\Pi = D\sigma_{eff}$. The results of such calculation, based on the solution of the diffusion equations with boundary conditions of the first kind, have shown[47] that the values of D and σ_{ef} vary non-monotonically as the thickness of the membrane is altered. Starting with $d = 2600$ μm, the diffusion coefficient increases sharply while the solubility coefficient diminishes. Such behaviour of D and σ_{eff} may be caused by the initial stages in the development of the convective movement indicated. By reducing diffusional restrictions, these movements diminish the solubility coefficients. The induced transport of CO_2 molecules through the membrane takes place with participation of the "carriers" of these molecules—HCO_3^- ions. The low rate constant for the dehydration reaction $HCO_3^- \rightarrow CO_2 + OH^-$ (10^{-4} s^{-1} [49] at pH > 8) can mean that the process has two rate-limiting stages—transport and chemical stages, whose characteristic times are comparable. Therefore the lifetime of these carriers may prove to be of the same order of magnitude as their residence time in the region of the liquid–gas interface, which ultimately diminishes σ_{eff}.

The liquid and also quasi-liquid membrane described are characterised by a unique selective permeability to CO_2. Thus the ratio α of the permeability constants of such membranes for CO_2 and O_2 is $\sim 10^2 - 10^3$. Despite the fairly large number of studies devoted to gas transport processes through quasi-liquid membranes, the question of the contribution of the individual stages of these processes (diffusion, solubility) to the establishment of the high selective permeability of the membrane to CO_2 nevertheless remains obscure. Furthermore, the influence of the inert base on the kinetic characteristics of quasi-liquid membranes and on the methods of stabilisation of these characteristics has not been elucidated.

An attempt to find an answer to these questions has been made in a study[47] of inert, alkali-resistant polymeric matrices into which solutions of 3.2 *N* Cs_2CO_3 and a catalyst (0.25 *N* Na_3AsO_3) had been introduced. The choice of these particular substances (whose concentrations correspond to the saturation of the solution by caesium bicarbonate when CO_2 is passed through) is determined by the high gas permeability coefficients of such membranes. Hydrophilic porous filters based on UEM-270 ethylcellulose with an average pore diameter $I = 27$ nm and a thickness $d = 72$ μm, and also the polysulphone UPM ($R = 50$ nm, $d = 100$ μm) and poly(vinyl chloride) ($R = 170$ nm, $d = 100$μm) have been used as polymeric matrices.

The relative pore volume was estimated from the difference between the weights in the moist and dry states and was found to be 73% for UEM-270, 58% for UPM, and 76% for PVC.

The corresponding $\sigma_{eff}(P)$ relations were calculated from the experimental[47] permeability coefficients Π and the effective diffusion coefficients D of carbon dioxide in quasi-liquid membranes and a number of conclusions were reached.

1. The carbon dioxide sorption isotherms (the dependence of the amount of CO_2 absorbed by the carbonate solution on its partial pressure in the gaseous mixture) is significantly non-linear and is almost independent of the nature of the polymeric matrix of the membrane.

2. The diffusion coefficient D increases with increase in the CO concentration in solution and depends greatly on the average pore size in the initial matrix. For relatively small average pore dimensions (27 and 50 nm), D is almost constant. However, the increase of R from 50 to 170 nm alters D almost by a factor of 5. Such behaviour of the diffusion coefficients can be explained by the appearance in the large pores of a kind of convective displacements of the structural units of the solution (associated ions and water molecules) as a consequence of the local heating of the solution during the course of the binding of CO_2 molecules.

3. The character of the variation of the permeability coefficient Π as the carbon dioxide pressure in the initial mixture is varied is associated with the antiparallel dependences of D and σ on P.

In conclusion of the Section, we shall discuss factors determining the high selectivity of the quasi-liquid membrane. The permeability, diffusion, and solubility coefficients of carbon dioxide and oxygen in the UEM-270 porous filters saturated with distilled water or the 3.2 N Cs_2CO_3 + 0.25 N Na_3AsO_3 solution are presented below (for $P_{CO_2} = P_{O_2} = 100$ kPa[47]):

		$10^{13}\Pi$, mol s^{-1} m^{-1} Pa^{-1}	$10^{10}D$, m^2 s^{-1}	$10^{4}\sigma$, mol m^{-3} Pa^{-1}
CO_2	H_2O	1.48	4.05	3.65
CO_2	3.2N Cs_2CO_3+0.25N Na_3AsO_3	2.74	$2.4\cdot10^{-2}$	$1.14\cdot10^{3}$
O_2	H_2O	$5.51\cdot10^{-3}$	4.0	$1.38\cdot10^{-1}$
O_2	3.2N Cs_2CO_3+0.25N Na_3AsO_3	$1.7\cdot10^{-3}$	$2.7\cdot10^{-1}$	$6.3\cdot10^{-3}$

For a membrane containing distilled water, $\alpha \simeq 27$. The selectivity of a quasi-liquid membrane increases to 160.

The example considered makes it possible to understand how high selectivity coefficients of liquid and quasi-liquid membranes can be attained and what are the possible ways of increasing the permeability to the target components. Here it is naturally necessary to achieve the stability of such systems, which may become a complex problem in their practical employment (for example owing to ageing or the elution of the reagents from the quasi-liquid membrane, as a consequence of the poisoning of the complex-forming carrier, owing to difficulties in its regeneration, etc.).

Microporous polypropylene,[50] polytetrafluoroethylene, poly(vinyl chloride), and polysulphone,[51] used in ultrafiltration and microfiltration processes, serve nowadays as bases for quasi-liquid membranes. Impregnation of such filters with liquid reactive carriers makes it possible to obtain membranes for the effective separation of liquids and gaseous mixtures combining the high efficiency of the porous membranes with the high selectivity of the carrier.[52–54] We may point to advances in the creation of highly selective membranes for the isolation of oxygen from air (the ratio of the corresponding permeability constants is $\sim 26-50$) which permitted the attainment of a nitrogen content in oxygen of only 9–15% after a single-stage separation.[55]

Liquid membranes of the emulsion type, stabilised by surfactants, have already found application in industry. In particular, the effectiveness of the use of such systems for the isolation of zinc[56] and sodium[57] ions, enzymes,[58] copper,[59] phenol,[60] and other organic and inorganic substances has been demonstrated (see also Van et al.[61]).

5. Membrane Processes Involving the Isolation of Vapour Mixture Components

New possibilities of the isolation of vapour components from liquids and vapour–gas mixtures have usually been attributed to the development of a new membrane process – membrane distillation.[62,63] We shall consider initially the simplest model ideas about the character of the movement of the gaseous mixture in porous systems in relation to transport in a straight cylindrical capillary.[64]

The movement of gases in such a capillary is determined by the Knudsen parameter Kn – the ratio of the number of collisions of the molecules with the walls to the number of intermolecular collisions. To within a constant multiplier of the order of magnitude of unity, the parameter Kn is equal to the ratio of the average length of the free path of the molecule l to the capillary diameter:

$$\mathrm{Kn} \simeq l/2r_c \qquad (17)$$

Since the lengths of the free path l_i of molecules in different gases in a gaseous mixture are of the same order of magnitude, the parameter Kn for a mixture of gases is approximately constant. Depending on the value of Kn, three characteristic gas flow regions are distinguished: the Knudsen region (Kn $\gg$ 1), the transitional region (Kn $\simeq$ 1), and the molecular region (Kn $\ll$ 1).

For Kn $\gg$ 1, the components of the gaseous mixture move through the capillary almost independently of one another. The total molar flux of the ith component under the conditions of Knudsen flow is therefore proportional to the gradient dc_i/dx of the molar concentration c_i of the component (the x axis is directed along the capillary axis):

$$J_i = c_i v_i = -D_i^K \frac{dc_i}{dx} = -D_i^K \left[c \frac{dy_i}{dx} + y_i \frac{dc}{dx} \right], \quad y_i = c_i/c, \; c = \sum_i c_i \qquad (18)$$

where D_i^K is the Knudsen diffusion coefficiient, c the total molar concentration, and v_i the velocity of the ith species along the capillary. For a cylindrical capillary under the conditions of diffuse reflection of the species from the walls (accommodation coefficient $\gamma_{a,i} = 1$), we have

$$D_i^K = \frac{2}{3} r_c \bar{w}_i \qquad (19)$$

where $\bar{w}_i = (8k_B T/\Pi m_i)^{1/2}$ is the average thermal velocity of type i molecules. If there are N such cylindrical pores per unit surface of the membrane, then the permeability constant Π_i of this membrane for type i molecules can be represented in the following form taking into account Eqn.(19) and the equation of state of an ideal gas:

$$\Pi_i = \frac{8R^3 N}{3N_A} \left(\frac{\pi}{2m_i k_B T} \right)^{1/2} \qquad (20)$$

where N_A is the Avogadro number.

The relationship (Kn $\ll$ 1) obtains in fairly broad capillaries. The average linear velocities of the components are then constant along the section of the capillary, while the molar fluxes are related to the gradient of the driving forces by the Stefan–Maxwell system of equations. For constant P and T and also in the absence of external

forces, the Stefan–Maxwell system of equations can be conveniently put in the form

$$\frac{dc_i}{dx} = \sum_{i \neq j} (c_i J_j^{T,P} - c_j J_i^{T,P})/D_{ij}c \quad . \tag{21}$$

Here $J_i^{T,P}$ is the molar flux of the ith component for constant P and T and D_{ij} is the mutual diffusion coefficient of components i and j. Here we may note one non-trivial factor. Under the conditions of isobaric-isothermal molecular flow (Kn $\ll$ 1) of a mixture of gases in a long capillary, the interaction of the gas with the walls also proves very significant, since it determines the inter-relation between the partial fluxes. In order to obtain the corresponding conditions, we shall take into account the fact that, for a zero pressure drop across the capillary, the overall momentum $M_\parallel$, transmitted to the walls of the capillary when all the molecules of the mixture interact with them is zero:

$$M_\parallel = \sum_i M_{\parallel,i} = 0 \ , \tag{22}$$

$$M_{\parallel,i} = \frac{1}{4} c_i \bar{w}_i m_i v_i (r_c) \gamma_{a,i} \ .$$

Taking into account the relation $w_i \propto m_i^{-1/2}$, we find from Eqn.(22) the expression

$$\sum_i m_i^{1/2} \gamma_{a,i} J_i^{T,P} = 0,$$

which yields the required relation for the case of the diffuse reflection of the component or for the independence of the coefficient $\gamma_{a,i}$ of the type of species:

$$\sum_i m_i^{1/2} J_i^{T,P} = 0 \tag{23}$$

This is the so called Graham condition.[65]

In the case of a binary gaseous mixture with P = const. and T = const., we obtain from Eqns.(21) and (23)

$$J_i^{T,P} = D_{ij}(1 - \alpha_{ij} c_i/c)^{-1} \frac{dc_i}{dx} = -D_{ij} c (1 - \alpha_{ij} y_i) \frac{dy_i}{dx} \ , \tag{24}$$

where $\alpha_{ij} = 1 - (m_j/m_i)^{1/2}$. Eqn.(24) has the form of Fick's law only for a small mole fraction ($y_i \ll 1$) of the diffusing component (diffusion of an impurity) or for the diffusion of components with the same molecular weights ($m_1 = m_2$); in the latter case $J^{P,T} = J_1^{P,T} + J_2^{P,T} = 0$.

The transitional regime (Kn $\simeq$ 1) in the flow of a gaseous mixture in capillaries is significantly more difficult to investigate. In the corresponding analysis, one usually employs interpolation formulae. The expression for the partial flux in the case of isobaric-isothermal flow of the binary mixture is usually represented in the form

$$J_i^{T,P} = -D_{b,ij} c \frac{dy_i}{dx} \tag{25}$$

and the Bosanquet expression [64] is used for $D_{b,ij}$—the binary diffusion coefficient in the transitional regime:

$$D_{b,ij}^{-1} = \frac{1}{D_i^K} + \frac{1 - \alpha_{ij} y_i}{D_{ij}} \tag{26}$$

When transport in a porous medium is considered, the coefficients D_i^K and D_{ij} are usually renormalised by introducing into them the multiplier ε/ζ, where ε is the velocity of the material and ζ the tortuosity of the pores.

The above expressions for the fluxes of the components of gaseous mixtures in capillaries in different flow regimes can be used for the analysis of the problems of the membrane separation of gaseous and vapour–gas mixtures. In the first place, we have in mind here the Knudsen flow regime in which the mixture of gases passing through a porous membrane is enriched, in accordance with Eqn.(20), in the lighter components. However, such processes are not sufficiently effective owing to the relatively small mixture separation factors in cases of greatest practical interest. Admittedly, in the membranes with a continuous diffusion layer employed for technological purposes, the possibility of the existence of "through" submicrodefects and transport via such defects must be taken into account in accordance with the formulae quoted above.

The calculation of gas fluxes in capillaries is of greater current interest in connection with the development of the physicochemical principles of membrane distillation. This process consists in the selective mass transfer of water vapour through a finely porous hydrophobic membrane separating two aqueous solutions whose temperatures are different. The vapour molecules are transferred from the heated surface of the aqueous solution through the membrane pores and are concentrated on the cooled side. Evidently, the above process can find practical application (purification of sewage, desalination, concentration of solutions) in those cases where the cost of setting up a temperature gradient on the membrane is low (for example, when waste heat from industrial manufacturing processes is used). In the desalination of an NaCl solution, the flux $J = 3 \times 10^{-2}$ m^3 m^{-2} day^{-1} when the temperature difference between the two sides of a porous polypropylene membrane $\Delta T = 10$ K.[63] One of the advantages of the above process over distillation is the possibility of carrying it out for small temperature differences.

At the present time the membrane distillation method is used successfully not only for the purification of aqueous solutions with involatile solutes (salts, glucose) but also for the separation[69] and concentration[70] of mixtures (water–alcohol mixtures, for example) when all the components are volatile. Under these conditions, together with the traditional versions of the method, new ones are investigated:[69,71,72] membrane distillation with evaporation into a vacuum and membrane distillation with an air gap or "thermal evaporation" through a membrane (a distillate from a 3.4% aqueous NaCl solution has been obtained by this method[71]). In the application of the latest versions, the efficiency of the process increases significantly as a result of the possibility of maintaining a larger temperature difference.

Evidently, the methods indicated make it possible to achieve effective evaporation through porous membranes in contrast to the traditional processes involving evaporation through non-porous polymeric membranes.[35,36,73] However, the traditional method has not lost its importance, especially in connection with the development of the new membrane materials,[74] which retain their separating characteristics in the course of prolonged use. In evaporation through a non-porous membrane, the driving force of the process is the difference between the chemical potentials of the substance on the two sides of the membrane. The permeating substance is removed in the vapour phase by creating a vacuum or together with a stream of inert gas.

Like the membrane gas separation process, this process ensures a high degree of separation in a single stage at a relatively high flow rate through the membrane. It can be used for the separation of mixtures of hydrocarbons and aqueous organic mixtures and also for the dehydration of solutions. The possibility of separating with its aid azeotropic mixtures and mixtures with similar boiling points and solubilities is of greatest value. Since the efficiency of the separation in evaporation through a membrane is determined by the permeability constants, i.e. the products of the diffusion coefficients of the components and their thermodynamic solubilities, it follows that, in order to increase the selectivity of the transport, it is desirable to

introduce into the polymer matrix functional groups capable of interacting strongly with individual components of the mixture to be separated (for example, the introduction of electron-donating groups in the presence of electron-accepting molecules in the mixture[75]). This makes it possible to attain a high process selectivity (including the possibility of separating isomers[75]) by varying the chemical composition and structure of the polymeric selective layer in the composite membranes usually employed for such purposes (together with asymmetric polysulphone membranes). The idea of imprinting[76] (preliminary "tuning") of the polymer matrix with respect to species of a specific type, which increases the degree of selective sorption of the given component, is especially promising in this instance (as in reverse osmosis and gas separation processes).

We may also point to studies of the removal of traces of organic substances (chloroform, trichloroethylene, etc.) from water[77] and of the separation of water–alcohol[78,79] and other aqueous organic mixtures.[80,81] Composite membranes with a selective layer based on polyamidoimides and polyamides are effective for the separation of mixtures of water with acetic acid.[82]

In conclusion of this Section, we shall deal with the interesting phenomenon of the oscillation of the permeability and selectivity with respect to components migrating through a membrane, which has been observed in the evaporation of an aqueous solution containing 10 vol.% of isopropyl alcohol through an asymmetric polyvinyltrimethylsilane (PVTMS) membrane with a thickness of the active diffusion layer of 0.2 μm.[83] The experimental apparatus consisted of a thermostatted cell with a membrane fixed with a vacuum tight joint. On the side of the diffusion layer, the membrane was in contact with the liquid and on the opposite side there was a chamber, evacuated to a residual pressure of 0.1–1.0 Pa, containing a trap cooled with liquid nitrogen. In order to avoid concentration polarisation, the liquid was thoroughly stirred. The flux density was calculated from the mass of the condensed vapour which had passed through the membrane and its composition characterised the selectivity of the membrane. The amount of evaporated liquid constituted only a very small fraction of the initial amount, so that its concentration remained almost constant throughout the experiment. The auto-oscillatory regime was established after an induction period. Alcohol and water evaporated preferentially for the minimum and maximum flux density through the membrane respectively.

According to Ageev and Sekacheva,[83] the mechanism of the observed process is as follows. According to the conditions governing the formation of asymmetric membranes, internal stresses arise in the active PVTMS layer. When the polymer comes into contact with the solution of the alcohol, whose molecules in this case play the role of a surfactant, the strength of the membrane diminishes and the stretching forces due to the internal stresses become capable of causing local disruption of the material with formation of microcracks directed into the interior of the membrane. The surfactant migrates preferentially from the solution into the zone of the microcrack, since it is sorbed by the hydrophobic polymer significantly more effectively than water; this promotes the growth of the microcrack to a micropore characteristic of the porous layer of an asymmetric membrane. The stretching and compressing internal stresses diminish under these conditions. The walls of the micropore formed are "lined" with the surfactant, whose molecules are linked to the non-polar polymer via their hydrophobic component, while the hydrophilic component is oriented towards the body of the pore. The imparting of hydrophilic properties to the surface of the micropore promotes preferential transport of water molecules and an increase in the overall flux as a consequence of the decrease in the activation energy for the transmembrane transport. The increased water concentration in the pores induces the desorption of the surfactant, an increase in surface tension, and hence an increase in cohesive forces. The latter tend to decrease the surface area and the structure becomes continuous again. The collapse of micropores increases the stretching snd hence the compressing internal stresses. The mechanism of mass transfer changes to an activated one, which leads to the preferential migration of the surfactant and the process is repeated. Thus the oscillations in the flux and concentration are accompanied by oscillations in the internal stresses. As the internal stresses relax, the oscillations should decay. The oscillation period is related to the time of structural transitions which is controlled by the kinetics of the sorption and desorption of the surfactant.

The mechanism described can be regarded as the manifestation of the Rebinder effect in polymeric systems. Reversible structural transitions play in this instance the role of a kind of feedback relay issuing commands to include and exclude non-activated flow stages, which in fact leads to the oscillatory regime in the operation of the membrane. The corresponding mathematical procedures, adequately representing the phenomenon described, have been developed.[84]

IV. MEMBRANE CATALYSIS

New possibilities in the application of membrane technology are associated with the development of membrane catalysis – the creation of chemical reactors in which catalytic reactions on the surface or in the bulk of the membrane are combined with the simultaneous controllable supply of the initial reactant (frequently in a specified "activated" form) through the membrane to the reaction zone or the removal of the products from the reaction zone (situation characteristic of native system "bioreactors"). The possibilities of the selective transfer of the reactants or products through the membrane are naturally related to the difference between the permeability constants $\Pi_i = D_i\sigma_i$ for individual components.

Membrane catalysis was first applied in the hydrogenation reactions of hydrocarbons and the reaction of carbon monoxide with hydrogen using membrane catalysts made of palladium and its alloys.[85] The efficiency of such processes is determined by the high permeability of palladium membranes to hydrogen and the formation on their surface of catalytically active adsorbed atomic hydrogen.[86] Not only the catalytic activity of the catalyst but also the flux of hydrogen atoms arising from the bulk of the membrane to the surface (the atoms can carry a small effective charge[87]) depends on the state of the catalyst surface.

The use of membrane catalysts based on palladium and its alloys and also silver and nickel makes it possible to carry out various processes of practical importance with a high degree of efficiency: hydrogenation of acetylene to ethylene, of diene hydrocarbons to olefinic hydrocarbons, and of naphthalene to tetralin, dehydrogenation of alkenes and alkanes, etc. (see the articles contained in the compendium edited by Gryaznov and Klabunovskii[85]).

Membrane catalysts based on transition metal and rare metal oxides exhibiting a higher ionic conductivity at elevated temperatures have begun to be developed in recent years.[85–94] A wide-scale search is being prosecuted at the present time for systems of this kind, used in the first place for the oxidation of organic compounds. Processes involving the oxidation of ethylene[89] and propene[90] to the corresponding epoxides with separation of oxygen and the initial

hydrocarbon on the membrane, which was based on yttrium-stabilised zirconium oxides deposited on a porous silver catalyst, have been carried out. The O^{2-} ions are electrochemically "pumped up" through the solid electrolyte to the catalyst. The selectivity of this process is appreciably higher than in the case where molecular oxygen is supplied to the system (without "pumping" O^{2-}). When scandium- or yttrium-stabilised zirconium oxides were used as the solid electrolyte (membrane), it was possible to achieve also the oxidative dehydrogenation of ethylbenzene.[91] The removal of oxygen from platinum and gold catalysts significantly increased the rate of decomposition of NO.[92] Analogous studies have been carried out on the oxidation of SO_2,[93] the electrochemical oxidation of H_2, CO, and CH_4,[94] etc.

In a number of studies bismuth oxide stabilised by the addition of other oxides was used as the solid electrolyte. Such systems are stable up to 800 °C and exhibit a high conductivity with respect to oxygen ions.[88] In particular, the $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ system has been used not only as a membrane separating atmospheric oxygen from the given reagent (propene in helium) but also as the catalyst of the oxidative dehydrodimerisation of propene.[88] Dissociative adsorption and reduction of molecular oxygen take place on the catalyst surface on the air side; the oxygen ions then migrate to the opposite side of the catalyst membrane where they substitute the ions of the lattice oxygen functioning as the oxidant. The selectivity in the formation of C_3 dimers was greater than in the case where oxygen and propene were supplied from one side; there is no loss of catalytic activity if the rate of the process is limited by the supply of oxygen ions to the reaction surface.

There is no doubt about the likely usefulness of such research, because an increase in the process selectivity frequently plays a decisive role in the assessment of the economic value of a particular method of synthesis of the required product. Further progress will also be associated with the determination of the nature of the catalytic effect in the reactions investigated, the establishment of the role of promoting additives, and the search for methods for additional activation of the catalyst surface.

The nature of the catalytic activiy of solid-phase systems is associated primarily with the specific features of the submicrostructure in the catalyst regions near the surface (characteristic size $\sim$1–10 nm) and with the distortion of the equilibrium configuration of the ligands and hence with the decrease in the symmetry of the local environment of the "active centre", which may be a transition metal ion or group of ions. The symmetry of the crystal field acting on such a centre is then reduced compared with the symmetry typical for an equilibium matrix. As a consequence of this, the parameter Δ of the splitting of the *d* levels of the transition metal ion in the active centre diminishes, which leads to a rearrangement of the electron sybsystem of the centre and an increase in the fraction of the high-spin state of the ion with an increased catalytic activity.[95]

Apart from structural factors, the chemical activity of the surface layers of the solid-phase matrix can depend significantly on its dynamic properties. In the region of structurally non-equilibrium fragments, the vibrational relaxation time of the local thermal excitations,[96] whose energy exceeds the strain energy of the structurally non-equilibrium matrix, can be significantly retarded. For this reason, catalytic reactions in the course of which thermal energy is locally evolved and there is a possibility of a rearrangement of the matrix, can exert an additional influence on the activated processes occurring in the matrix, including their influence on the kinetics of the catalytic processes proper, and can lead to a non-Arrhenius character of the temperature variation of the rate constants.[11,12,96]

We may also note the role of the conformational mobility of the structural fragments in the region of the active centre, which is responsible for the increase in the entropic factor governing the rate constant for the elementary reaction and increases the probability of the realisation of the "lock and key" relationship in the substrate–active centre system.[97]

All the factors indicated can influence the kinetics of the catalytic reaction on the surface of an inorganic membrane and further experimental studies promoting the elucidation of the role of each of them are therefore essential (the application of Mössbauer spectroscopy for this purpose is extremely effective[95,97]).

One may note yet another factor which is important in the analysis of the catalytic process with participation of oxygen – the presence of different, in the simplest case two, forms of adsorbed oxygen: the weakly chemisorbed (non-reconstructive) form, exhibiting as a rule an increased reactivity,[98,99] and the "deep (reconstructive) form of adsorption" involving stronger binding to the surface.[99] These forms obtain in the adsorption of oxygen both on oxide and metallic catalysts.[100–102] It has been suggested that the formation of these forms is due to adsorption on different active centres of the surface. One cannot rule out also another possibility – the formation of metastable adsorbed forms in adsorption on a single centre (for further details, see Savchenko[99]).

The quantum-chemical nature of the dual character of the adsorption of certain molecules on the same centres can be understood if account is taken, following Balabanov et al.,[103] of the exponential decrease in the intensity of exchange adsorbent–adsorbate interaction (the resonance integral) with increase in the distance of the adsorbate molecule from the catalyst surface. Here the energy of the ground state of the system is characterised by two minima located at different distances from the geometrical surface of the adsorbent and to which correspond bonds with different amounts of ionic character (a more covalent bond corresponds to a minimum at a greater relative distance). The above states of the molecule in adsorption can correspond to these minima: "closely bound" molecules and molecules adsorbed on the "outer surface" of the adsorbent (the weakly chemisorbed form). One of these states should be regarded as metastable. The appearance of a particular form of adsorption depends not only on the thermodynamic characteristics of the system but also on the adsorption conditions.

The formation of two forms of oxygen chemisorbed on metals has been considered.[101,104] As an example, we shall consider the possible reorganisation of the initial electronic structure of the real surface of silicon (an adequate set of experimental data exist for the system) in its electrochemical formation (as a consequence of the adsorption of the oxygen of water[105]). The SiO^- bond formed at the SiO_2–electrolyte interface is shorter (its length is 1.55 Å) than the Si–O–Si bridge bonds, because the extra electron pair at the anionic oxygen atom promotes the overlap of the p_π orbits of oxygen and the unoccupied d_π orbit of silicon, i.e. an increase in the $Si-O^-$ bond order (which is close to two).[106] If the initial dipole moment of the surface is such that the negative pole is directed to the outside (of Mikhailovskii et al.[101]), then such "contact" dipoles (the "strong form of chemisorption") can lead to a decrease in the initial dipolar jump in the vicinity of the $Si-O^-$ dipoles, i.e. the deformation of "holes" in the initial dipolar layer; the electrostatic field of the $Si-O^-$ dipoles can suppress[107] the anodic process, namely it can release positively charged ions into the electrolyte from the surface layers of SiO_2. The possibility of "controlling" the kinetics of chemical reactions on the SiO_2 surface thereby arises, provided that they are associated with the transport of positively charged ions through the

SiO_2–electrolyte interface. Evidently, when the SiO_2 surface is formed in another way (in the absence of anodic polarisation), the $Si–O^-$ dipoles are not formed and a weak chemisorption form of the silicon–oxygen bond, activating the anodic process, arises.

Such opposite (or sharply different) influences of various forms of adsorption of molecules on the kinetics of interphase physicochemical processes occurring with their participation can apparently be regarded as a fairly general phenomenon. In particular, on the basis of the model proposed, ideas can be developed[108] concerning the dependence of the atomic catalytic activity on the amount of ionic character of the metal–oxygen bond and ways of increasing the catalytic activity of the catalysts, including membrane catalysts, can be sought by means of a specific treatment of their surfaces. Here one must bear in mind that additional heating with subsequent quenching can accelerate the activated transitions of molecules between different adsorption states[98] and, in particular, can activate the reactive forms.

Membranes obtained by immobilising fragments of biological systems (enzymes or whole bacterial cells) on inorganic and organic supports or on polymers of different nature have the most unique catalytic properties. The high efficiency of such systems is manifested in organic synthesis[109] and in biotechnology (the preparation of aliphatic acids and glycerol from vegetable oils,[110] the conversion of lactose into glucose and galactose,[110] the manufacture of caffeine,[111] antibiotics,[112] etc.).

Further progress in this direction will undoubtedly be associated with the discovery of methods for the stabilisation of the funcional characteristics of such membrane reactors and with the search for methods of intensifying the processes including the procedure involving a change in the conditions of such processes and in the external influences. The creation of jumps in the electrochemical potentials of different ions on either side of the basic synthetic membrane (of the type of the liposomal membrane), on which enzymes are immobilised, may prove effective. The opposed or unidirectional ionic fluxes ("antiport" or "symport") through the basic membrane arising in this instance alter the local composition of the electrolyte in the vicinity of the immobilised enzymes and thereby influence the rate of formation and the yield of the reaction products. The use of photodependent systems, in particular of bacteriorhodopsin in order to couple processes involving the utilisation of light energy and the enzymic reaction proper, appears promising.[113]

V. CONCLUSION

Evidently the advances in the construction and creation of membrane reactors for the solution of biotechnological problems will be determined by the advances in the study of not only the general principles but also of the details of the functioning of the native systems.

The investigation of ion and molecule transport processes in synthetic membranes can in its turn contribute new ideas to the understanding of the characteristics of the functioning of the native systems. As mentioned above, ionic transport in the channels of perfluorinated sulphonic acid cation-exchange membranes under the conditions of limited ion hydration can model the transport in the channels of biological membranes – the elementary jumps of the ions between adjacent functional groups. Studies on the transport processes in vitreous polymers make it possible to put forward hypotheses concerning the nature of the multilevel character of the conductivity of the native ionic channels. The study of the characteristics of ionic transport in synthetic membranes and of the effects of concentration polarisation in the regions of the electrolytes adjoining the membranes has created a basis for a number of hypotheses[1] about hitherto puzzling effects of the action of electromagnetic radiation on biological systems.[114]

In the analysis of the most complex and artificially non-reproducible biological phenomena, one must bear in mind the idea expressed by Frenkel':[115] "the more complex the system considered, the simpler should be, through necessity, its theoretical description ... a good theory of complex systems should constitute merely a good "caricature" of the systems, exaggerating their most typical properties and deliberately ignoring all other, insignificant properties". However, even in the creation of such "caricatures" a wide variety of models appear, which indicates the impossibility at the present time of identifying any unique fundamental schemes for the realisation of native processes. The clear inadequacy of the experimental data, especially under conditions *in situ*, must then be partly made good by intuitive ideas based on the knowledge of the physical chemistry of a wide variety of non-biological processes (catalytic, electrochemical, and mechanochemical). In the solution of the problems of the construction of bioreactors, the situation is somewhat simplified: there is no need to consider new concepts (apart from the known physicochemical ideas), because one is dealing with the characteristics of the functioning of only the individual units of complex biological systems and the most general problems of living organisms as essentially self-organising and self-developing systems are not involved.

The physical chemistry of the elementary processes in native and synthetic membranes is the same despite the immeasurably greater complexity of biological systems. Future advances in the sciences concerned with the study of transport processes *in vivo* and in artificial membranes, namely the understanding of the principles of the functioning of living systems and new practical achievements in mem-brane technology, can be seen to be engendered by the close inter-relation between such sciences.

REFERENCES

1. S.F.Timashev, "Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Membrannym Metodam Razdeleniya Smesei" (Abstracts of Reports at the IVth All-Union Conference on Membrane Methods for the Separation of Mixtures), Izd.NIITEKhIM, Moscow, 1987, Vol.1, p.1.
2. S.F.Timashev, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, pp.57, 110.
3. Yasuo Kagawa, "Biomembranes" (Translated into Russian from Japanese) (Edited by B.E.Kagan), Izd.Vys.Shkola, Moscow, 1985, p.303.
4. V.G.Ivkov and G.N.Berestovskii, "Dinamicheskaya Struktura Lipidnodo Sloya" (The Dynamic Structure of the Lipid Layer), Izd.Nauka, Moscow, 1981, p.293.
5. A.S.Davydov, "Biologiya i Kvantovaya Mekhanika" (Biology and Quantum Mechanics), Izd.Naukova Dumka, Kiev, 1979, p.296.
6. Yu.A.Ovchinnikov, N.G.Abdulaev, M.Y.Feigina, A.A.Kiselev, and N.A.Lobanov, FEBS Lett., 1979, **100**(2), 219.
7. D.M.Engelman, R.Henderson, A.D.McLachlan, and B.A.Wallace, Proc.Nat.Acad.Sci.USA, 1980, **77**, 2023.
8. R.H.Lozier, R.A.Bogomolni, and W.Stoeckenius, Biophys.J., 1975, **15**, 955.

9. W.Stoeckenius, R.H.Lozier, and R.A.Bogomolni, Biochim.Biophys.Acta, 1979, **505,** 215.
10. A.V.Maksimuchev, S.K.Chamorovskii, S.F.Timashev, et al., Biologicheski Membrany, 1984, **1,** 1290.
11. S.F.Timashev, "Fizikokhimiya Membrannykh Protsessov" (Physical Chemistry of Membrane Processes), Izd.Khimiya, Moscow, 1988, Chapter 1.
12. S.F.Timashev, "Vsesoyuznoe Seveshchaniya po Samorganizatsii v Fizicheskikh, Khimicheskikh i Biologicheskikh Sistemakh 'Sinergetika-86'" (All-Union Conference on Self-Organisation in Physical, Chemical, and Biological Systems "Sinergetika-86'), Izd.Shtiintsa, Kishinev, 1986, p.80.
13. S.F.Timashev, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.3.
14. S.S.Dukhin, N.V.Churaev, V.N.Shilov, and V.M.Starov, Uspekhi Khim., 1988, **57,** 1013 [Russ.Chem.Rev., 1988(6)].
15. B.V.Deryagin, N.V.Churaev, and V.M.Muller, "Poverkhnostnye Sily" (Surface Forces), Izd.Nauka, Moscow, 1985, 400 pp.
16. A.A.Ovchinnikov, S.F.Timashev, and A.A.Belyi, "Kinetika Diffuzionno-Kontroliruemykh Khimicheskikh Protsessov" (Kinetics of Diffusion-Controlled Chemical Processes), Izd. Khimiya, Moscow, 1986, 287 pp.
17. M.Kurihara, Y.Himeshima, and T.Uemure, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.428.
18. Yu.E.Kirsh and Yu.M.Popkov, Uspekhi Khim., 1988, **57,** 1003 [Russ.Chem.Rev., 1988(6)].
19. B.I.Shklovskii and A.L.Efros, Uspekhi Fiz.Nauk., 1975, **117,** 401.
20. A.S.Skal and B.I.Shklovskii, Fiz.i Tekh.Poluprovodnikov, 1974, **8,** 1586.
21. L.I.Kheifets and A.V.Neimark, "Mnogofaznye Protsessy v Poristykh Sredakh" (Multiphase Processes in Porous Media), Izd.Khimiya, Moscow, 1982, 320 pp.
22. A.V.Neimark, "Matematicheskie Metody Opisaniya Gornykh Porod i Rascheta Ikh Effektivnykh Svoistv" (Mathematical Methods for the Description of Rocks and the Calculation of Their Effective Properties), Izd.Nauka, Moscow, 1986, p.80.
23. D.S.Gaunt and M.F.Sykes, J.Phys.A., 1983, **16,** 783.
24. Yu.M.Vol'fkovich, V.S.Dubasova, and V.A.Ponomarev, Elektrokhimiya, 1982, **18,** 1148.
25. M.A.Krykin and S.F.Timashev, Vysokomol.Soed., 1988, **30A,** 21.
26. S.A.Stern, V.M.Shah, and B.J.Hardy, J.Polym.Sci.B.Polym. Phys., 1987, **25,** 1263.
27. K.Takada, H.Matsuya, T.Masudak, and T.Higashimura, J.Appl.Polym.Sci., 1985, **30,** 1605.
28. S.G.Durgar'yan, Yu.P.Yampol'skii, and N.A.Plate, Uspekhi Khim., 1988, **57,** 975 [Russ.Chem.Rev., 1988(6)].
29. P.P.Zolotarev and V.N.Ugrozov, Zhur.Fiz.Khim., 1983, **57,** 1490 [Russ.J.Phys.Chem., 1983(6)].
30. I.N.Bekman and I.P.Romanovskii, Uspekhi Khim., 1988, **57,** 944 [Russ.Chem.Rev., 1988(6)].
31. S.F.Timashev, Zhur.Fiz.Khim., 1983, **57,** 68 [Russ.J.Phys. Chem., 1983(1)].
32. V.A.Abdyukhanov and N.I.Nikolaev, "Tezisy Dokladov II Vsesoyuznoi Konferentsii po Membrannym Metodam Razdeleniya Smesei" (Abstracts of Reports at the IInd All-Union Conference on Membrane Methods for the Separation of Mixtures), Izd.VNIISS, Vladimir, 1977, p.54.
33. V.K.Belyakov, E.E.Khorunzhii, V.G.Karachevtsev et al., "Tezisy Dokladov III Vsesoyuznoi Konferentsii po Membrannym Metodam Razdeleniya Smesei" (Abstracts of Reports at the IIIrd All-Union Conference on Membrane Methods for the Separation of Mixtures), Izd.VNIISS, Vladimir, 1981, pp.319–320.
34. A.L.Karpova, E.A.Rozanova, V.E.Ostrovskii, and S.F.Timashev, "Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Membrannym Metodam Rasdeleniya Smesei" (Abstracts of Reports of the IVth All-Union Conference on Membrane Methods for the Separation of Mixtures), Izd.NIITEKhIM, Moscow, 1987, Vol.3, p.51.
35. M.A.Krykin, V.I.Volkov, I.P.Storozhuk et al., Khim.Fiz., 1986, **5,** 989.
36. M.A.Krykin, S.E.Sakharov, S.F.Timashev, et al., Khim.Fiz., 1986, **5,** 272.
37. S.F.Timashev, Dokl.Akad.Nauk SSSR, 1985, **283,** 930.
38. G.Eisenman, "Ion-Selective Electrodes" (Edited by R.A.Darts) (Translated into Russian), Izd.Mir, Moscow, 1972, p.11.
39. V.I.Volkov, I.A.Nesterov, S.F.Timashev, et al., "Tezisy Dokladov I Respublikanskoi Konferentsii po Membrannym Protsessam" (Abstracts of Reports at the Ist Republic Conference on Membrane Processes), Izd.IKKhKhV Akad.Nauk Ukrain.SSR, Kiev, 1987.
40. A.S.Skal, Zhur.Tekh.Fiz., 1981, **51,** 2443.
41. G.A.Yagodin and S.Yu.Ivakhno, Zhur.Vses.Khim.Obshch. im.Mendeleeva, 1987, **32,** 657.
42. V.V.Tarasov and A.A.Pichugin, Uspekhi Khim., 1988, **57,** 992 [Russ.Chem.Rev., 1988(6)].
43. N.N.Li, "Proceedings of a Seminar on Liquid Membrane Application in Waste Water Treatment and Metal Recovery", UMIST, Manchester, 1980, p.9.
44. L.Boyadzhiev, E.Bezenshek, and Z.Lazarova, J.Membr.Sci., 1984, **21,** 137.
45. A.A.Lev and E.P.Buzhinskii, Tsitologiya, 1967, **9,** 102.
46. V.V.Tarasov, G.A.Yagodin, and A.A.Pichugin, "Itogi Nauki i Tekhniki. Ser.Neorg.Khimiya" (Advances in Science and Engineering. The Inorganic Chemistry Series), Izd.VINITI, Moscow, 1984, Vol.11, p.171.
47. A.V.Vorob'ev, M.A.Krykin, Yu.M.Popkov, and S.F.Timashev, Teor.Osnovy Khim.Tekhnol., 1985, **19,** 675.
48. N.C.Otto and J.A.Quinn, Chem.Eng.Sci., 1971, **26,** 949.
49. D.M.Kern, J.Chem.Educ., 1960, **37,** 14.
50. D.Pearson, "Ion Exchange Membranes" (Edited by D.S.Flatt), Ellis Horwood, Chichester, 1983, p.55.
51. Y.Etoh, N.Ohashi, and C.Goto, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.819.
52. J.Matsuura, T.Oguchi, and M.Okada, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.781.
53. K.K.Sirker, R.Prasad, S.Majumdar, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.775.
54. T.Akedo and S.Manabe, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.779.
55. B.M.Johnson, W.W.Baker, S.L.Matson, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.596.

56. J.Draxler, W.Fursf, and R.Marr, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.789.
57. W.Yang, A.Yamauchi, and H.Kimizuka, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.791.
58. M.Dekker, K.Van't Reit, J.M.G.M.Wijnans, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.793.
59. C.C.Wang, D.L.Reed, and A.L.Bunge, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.785.
60. T.Kataoka, T.Nishiki, and S.Kimura, "The International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.795.
61. Z.Van, S.Li, L.Wang, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.777.
62. K.Schneider and T.I.van Gessel, Chem.Eng.Techn., 1984, **56**, 521.
63. E.Driolo and W.Yongle, "Membrane Phenomena and Processes", Technical University of Wroclaw, Wroclaw, 1986,
64. M.E.Findley, V.V.Tanna, Y.B.Rao, and C.L.Yeh, Amer.Inst. Chem.Engineers J., 1969, **15**, 483.
65. G.C.Sarty, C.Gostoli, and S.Matulli, Desalination, 1985, **26**, 277.
66. P.P.Zolotarev and S.F.Timashev, "Tezisy Dokladov I Respublikanskoi Konferentsii po Membrannym Protsessam" (The Abstracts of Reports at the Ist Republic Conference on Membrane Processes), Izd.IKKhKhV Akad.Nauk Ukrain.SSR, Kiev, 1987.
67. E.Ippert and P.Schneider, Chem.Eng.Comm., 1979, **3**, 65.
68. E.A.Mason, A.P.Malinauskas, and R.B.Evans III, J.Chem. Phys., 1967, **46**, 3199.
69. G.Sarti and C.Gostoli, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.488.
70. T.Nakane, H.Yanagishina, N.Tamura, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.588.
71. H.Kurokawa, A.Yamada, and S.Takahashi, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.582.
72. K.Ebara, H.Kurokawa, and S.Takahashi, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, 578.
73. Yu.I.Dytnerskii, "Membrannye Protsessy Razeleniya Zhidkikh Smes i" (Membrane Liquid Mixture Separation Processes), Izd.Khimiya, Moscow, 1975, 232 pp.
74. H.Strathman, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.20.
75. K.Ishihara, N.Suzuki, and K.Matusi, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.580.
76. B.Sellergen, "XXX Microsymposium on Macromolecules", Prague, 1987, p.31.
77. P.Aptel, A.Aurelle, Jl.Bersillon, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.487.
78. Q.T.Nguyen, A.Maazouz, and R.Clement, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.572.
79. X.Wei, J.Wanchang, L.Moe, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, 490.
80. W.Gudernatsch, H.Strathmann, and H.Chmiel, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.574.
81. J.Neel, Q.T.Nguyen, and R.Clement, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.479.
82. Z.Honda and Y.Maeda, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.482.
83. E.P.Ageev and N.V.Sekacheva, Vysokomol.Soed., 1985, **27B**, 163.
84. E.P.Ageev and A.V.Vershubskii, "Tezisy Dokladov IV Vsesoyuznoi Konferentsii po Membrannym Metodam Razdeleniya Smesei" (Abstracts of Reports at the IVth All-Union Conference on Membrane Methods for the Separation of Mixtures), Izd.NIITEKhIM, Moscow, 1987, Vol.2, p.66.
85. V.M.Gryaznov and E.I.Klabunovskii (Editors), "Metally i Splavy kak Membrannye Katalizatory" (Metals and Alloys as Membrane Catalysts), Izd.Nauka, Moscow, 1981, 181 pp.
86. Yu.M.Serov et al., Zhur.Fiz.Khim., 1986, **60**, 206 [Russ.J.Phys.Chem., 1986(1)].
87. "Vzaimodeistvie Vodoroda s Metallami" (The Interaction of Hydrogen with Metals), Izd.Nauka, Moscow, 1987, 296 pp.
88. R.Di Cosimo, J.D.Barrington, and R.K.Grasselli, J.Catal., 1986, **102**, 234.
89. M.Stoukides and C.G.Vayenas, J.Catal., 1981, **70**, 137.
90. M.Stoukides and C.G.Vayenas, J.Catal, 1983, **82**, 45.
91. J.N.Michaels and C.G.Vayenas, J.Catal., 1984, **85**, 477.
92. T.M.Gur and R.A.Huggins, J.Electrochem.Soc., 1979, **126**, 1067.
93. C.G.Vayenas and H.M.Saltsburg, J.Catal., 1979, **57**, 296.
94. R.A.Goffe and D.M.Mason, J.Appl.Electrochem., 1981, **11**, 447.
95. F.Kh.Chibirova et al., Fiz.Tverd.Tela, 1984, **26**, 890.
96. S.F.Timashev, Dokl.Akad.Nauk SSSR, 1987, **295**, 661.
97. F.Kh.Chibirova et al., Poverkhnost'. Fizika, Khimiya, Mekhanika, 1986, **10**, 888.
98. A.A.Slinkin et al., Kinetika i Kataliz, 1977, **18**, 742.
99. V.I.Savchenko, Uspekhi Khim., 1986, **55**, 462 [Russ.Chem. Rev., 1986(3)].
100. R.Kh.Burshtein et al., Zhur.Fiz.Khim., 1950, **24**, 214 [Russ.J. Phys.Chem., 1950(1)].
101. Yu.N.Mikhailovskii et al., Dokl.Akad.Nauk SSSR, 1979, **246**, 389.
102. M.E.Belyaeva and T.V.Kalish, Elektrokhimiya, 1979, **15**, 581.
103. B.I.Balabanov et al., Dokl.Akad.Nauk SSSR, 1978, **238**, 1365.
104. S.F.Timashev, Elektrokhimiya, 1979, **15**, 730.
105. S.O.Izidinov, Preprint 25-78, Siberian Division of the USSR Academy of Sciences, Novosibirsk, 1978.
106. M.G.Voronkov, Izv.Akad.Nauk Latv.SSR, Ser.Khim., 1961(2), 283.
107. S.F.Timashev, Zashchita Metallov, 1980, **16**, 176.
108. G.K.Boreskov, Kinetika i Kataliz, 1973, **14**, 7.
109. Y.Okahata and K.Ijiro, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.681.
110. G.Iorio, E.Drioli, and G.Catapano, "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.627.

111. M.Taya, M.Hegglin, K.H.Yoon, et al., "The 1987 International Conference on Membranes and Membrane Processes", Tokyo, 1987, p.629.
112. W.Klagba, J.Braun, and F.Le Goffic, "The 1987 International Conference on Membranes and Membrane processes", Tokyo, 1987, p.639.
113. A.V.Maksimychev and S.K.Chamorovskii, Uspekhi Khim., 1988, **57,** 1058 [Russ.Chem.Rev., 1988(7)].
114. G.Calacicco and A.A.Pilla, Bioelectrochem. and Bioenerget., 1984, **12,** 259.
115. Ya.I.Frenkel', "Na Zare Novoi Fiziki" (The Dawn of New Physics), Izd.Nauka, Leningrad, 1970, p.307.

Karpov Physicochemical Institute,
Moscow