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Ion transfer in ion-exchange and membrane materials

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Abstract. Modern concepts of mass transport in solids are considered. Essential information on the structure of organic and inorganic ion-exchange materials and on defect formation processes is presented. The key methods of investigations of ion transfer are described. The results of studies on the transfer processes in membrane systems induced by various driving forces including the concentration, electric potential and electrochemical potential gradients are generalised. The bibliography includes 530 references.

I. Introduction

Mass transport in solids and across their surfaces is of importance for separation and purification of liquids (including water treatment),[1–5] for fuel cell operation,[6] catalytic reactions,[4] as well as for numerous solid-phase,[7–9] sorption[4,10] and many other processes. Therefore, the problem of description of the kinetics of ion and molecular transfer has attracted the attention of researchers. However, no general approach to the solution of this problem has been proposed as yet notwithstanding its obvious importance and topicality. For each particular case there are specific relations, methods and terminology. As a consequence, researchers who study the mass transport problem in a certain field often have almost no information on the studies carried out by their colleagues in allied sciences. Narrow specialisation is also determined by the extreme complexity of phenomena accompanying the ion and molecular transport, *e.g.*, sorption and desorption of substances, defect formation in the interior and on the surface of ion-exchange materials (ion exchangers) and occurrence of chemical reactions. Mass transport can also be affected by the dimension of the system under study and by the possibility for transfer to follow alternative routes.[11,12] Therefore, often the kinetic laws that are successfully used for description of ion transport in a particular system can appear to be inapplicable to its close analogues. Nevertheless, the existence of some general regularities of the transfer processes occurring in solid systems of various nature seems not to be improbable. This requires the development of general approaches to the description of the chemical kinetics of ion transfer. Solving this problem has been the focus of considerable research involving a wide use of modern experimental equipment, theoretical concepts and various methods of numerical analysis.

The main goal of this review is to generalise approaches to the description of transfer processes in ion-exchange and membrane materials of various nature and to outline the main methods of investigations of ion transfer in such systems. In presenting the material the authors of this review tried to avoid the use of complicated mathematics. The emphasis is placed on consideration of relatively simple approaches and relations, on interpretation of the results obtained and on the description of regularities of transport processes in both organic high-molecular-mass and inorganic materials including systems possessing ion-exchange properties and ionic conduction.

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II. Structure of ion-exchange and membrane materials

1. Structure of organic ion-exchange materials

Currently, organic ion-exchange and membrane materials are used much more widely than their inorganic analogues. Therefore, most of the modern models of transfer and structure of ion-exchangers have been developed for organic materials. In this connection it is appropriate to consider first the structure of polymer-based materials. Ion-exchange materials of different nature including the so-called homogeneous membranes and gel ion exchangers are in fact inhomogeneous.[1,11–13] There are different forms of inhomogeneity, *e.g.*, a structural, chemical and physical one, which can manifest themselves on both the macro- and microscopic level. Sometimes, such inhomogeneities are created in a targeted manner in the course of synthesis procedures (macroporous ion exchangers, granulates, heterogeneous membranes). In other cases they appear spontaneously. Inhomogeneity of a material strongly affects the transfer mechanism and many physicochemical properties of ion exchangers, as well as the operating characteristics of membrane systems.

An ion exchanger, which is in equilibrium with atmosphere, is called dry (air-dry). However, even in this case the material contains some amount of water (nearly two water molecules per

ionogenic group for sulfonated cation exchanger and 3 mass % or about 2 %–3% of the maximum water uptake for perfluorocarbon membranes).[13, 14] The structure of the dry ion exchanger is determined by conditions of the polymer synthesis and by structural rearrangement of the polymer due to the presence of ionogenic groups.

If ion exchangers are obtained by polymerisation and polycondensation, small highly cross-linked nuclei are first formed. Then nuclei merge together, thus forming an island structure;[11] the process can be accompanied by entanglement of polymer chains.[12] As a consequence, the polymer contains a large number of defects of various nature and size. These defects impart different levels of heterogeneity, from microscopic (atomic groups and molecules) to macroscopic (macropores, clusters of size 100 nm and larger), to the polymer structure.

In numerous studies carried out since the mid-1950s pores and other features of the heterogeneous structure of polymer matrices were detected both by direct observations (by electron microscopy, scanning electron microscopy,[12] small-angle X-ray scattering,[13–16] Mössbauer spectroscopy,[13, 17, 18] NMR spectroscopy[19–22] and other methods[13, 20, 21, 23–28]) as well as by indirect measurements (by mercury porosimetry,[29] reference porosimetry,[30–32] differential scanning calorimetry,[33, 34] *etc.*[1, 34–37]).

Among the pioneering studies on the effect of charged ions on the ionomer structure was that reported by Eisenberg.[38] He chose an ion pair (an ionogenic group, *i.e.*, a partially or completely dehydrated fixed ion – counterion pair) as the main structural unit and showed that the dipole – dipole interaction causes association of the ion pairs to form the so-called multiplets containing no polymer chain segments. Due to steric hindrances the number of ion pairs in a multiplet is small, at most 6 – 8 according to Weiss *et al.*[39] and 2 according to Dreyfus.[40] The dipole – dipole attraction leads to aggregation of multiplets to yield larger associates (clusters). However, clustering induces a strong stretch of the elastic polymer matrix. The possibility for such a transformation to occur depends on several factors, *e.g.*, elasticity and degree of cross-linking of the polymer chains, concentration of ionogenic groups, *etc*. Ponomarev and Ionova[41] studied changes in the strain energy, the energy of hydrophobic interactions between polymer chains and the Coulombic interaction energy upon clustering of ionogenic groups and showed that the process is energetically favourable if the concentration of ionogenic groups is not too low and the polymer network is sufficiently elastic. The newly formed cluster acts as an additional cross-link, thus making the polymer matrix more rigid.

Dreyfus[40] considered a simple model, which allows assessment of the structure and estimation of the size of dry clusters, as well as determination of their arrangement in membrane (Fig. 1). The model assumes an ideal flexibility of polymer chains. The only factor which limits an increase in the density of ionogenic groups is the size of the polymer chains. For perfluorocarbon membranes the radius of the dry ionic cluster is 1 – 2 nm.[40] This is in agreement with the results of the small-angle X-ray scattering experiments.[15]

Hydration of ion exchangers causes essential changes in their structure. A consequence of hydration of ions and hydrophilic regions of the polymer matrix is swelling of the ion exchanger. This leads to an increase in the mobility of polymer chains, which, in line with the formation of a network of hydrogen bonds, facilitates additional aggregation and brings about clustering and formation of other structural elements with more or less homogeneous structure and composition. Because of this in studies on membrane systems such aggregates are called 'phases'. In spite of the fact that this term is not rigorous, we will use it in the text below. One phase is the hydrophilic 'gel' phase, which comprises the system of micropores formed by the rather closely spaced fixed and mobile ions and hydrophilic segments of the polymer chains. The second, hydrophobic, phase includes aggregated hydrophobic polymer chains and their bundles, as well as segments of an inert binder (*e.g.*, polyethylene), which is added to increase a membrane's mechanical strength. The electrically neutral solution, which fills voids, mesopores and macropores upon swelling, can be treated as the third phase.

As perfluorocarbon sulfonated cation-exchange membranes pass from the dry state to the swollen state with a water content of 20 mass %, the intensity of small-angle X-ray scattering by clusters increases by nearly an order of magnitude.[13] The intercluster distance increases from 2 – 3 to 4 – 5 nm.[13, 15, 42–44] Analogous results were obtained[16] for polyphosphazene membranes (a promising material for fuel cell applications).[45] As water penetrates into the cluster, its volume increases, thus causing a stretch of the elastic matrix. In this case hydrophobic segments of polymer chains can be displaced from the cluster volume, thus forming the hydrophobic phase. Equilibrium is attained when the energy liberated upon hydration of ions becomes equal to the energy required to stretch the matrix.[42–44, 46] As a result, the hydrated cluster looks like an inversed micelle.

The cluster – network model proposed by Gierke *et al.*[42] treats spherical clusters. The fixed ions are at the cluster's periphery, which provides a minimum value of the surface energy and excludes contact of the polymer with water. Counterions neutralise the charge of the fixed ions, thus forming an electrical double layer (Fig. 2). The interior of the cluster is filled with aqueous electrolyte solution. For simplicity, Hsu and Gierke[42] assumed that, depending on the energy state, there are two kinds of water, the 'inner' water and the 'surface' water. The latter fills the first and second outer layers of the cluster and constitutes the hydration shells of the fixed ions and counterions. The state of the inner water does not differ from the state of water in free solution.

The cluster diameter can be evaluated from the water uptake of the membrane. Assuming that clusters occupy the sites of a cubic lattice separated by 5 nm, the number of clusters per cubic centimetre of the membrane is 8×10^{18} while the number of water molecules per cluster at a water content of 15 vol. % is nearly 10^3. At a membrane capacity of 1 mmol cm^{-3}, the number of fixed ions in the cluster approaches a value of 70. The cluster diameter is

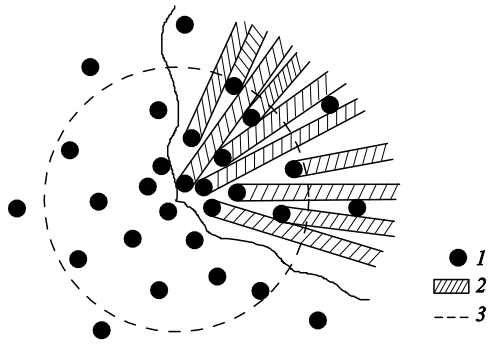


Figure 1. Schematic representation of a dry cluster in an ion-exchange membrane containing elastic hydrophobic polymer chains.[40]
Multiplets (*1*), polymer chain segments or bundles (*2*) and approximate cluster boundary (*3*).

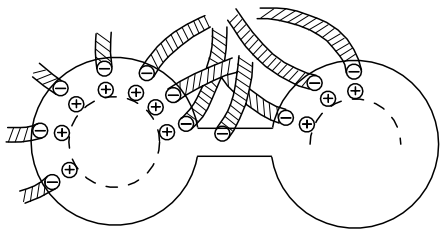


Figure 2. Schematic representation of the structure of a swollen perfluorinated membrane according to the cluster – network model of Gierke.[42]

$\sim$4 nm.[42] It increases as the membrane's exchange capacity increases and as the degree of cross-linking of the polymer matrix decreases.[15, 16]

This model also permits consideration of channels connecting adjacent clusters (see Fig. 2). Such channels were shown to be thermodynamically stable.[42] However, the free energy of the system changes only slightly upon channel formation (-11 J cm^{-3}); therefore, channels continuously appear and disappear. According to Timashev's figure of speech,[13] they are 'scintillating'. The calculated channel diameter (1.4 ± 0.2 nm) is consistent with the experimental data (1.2–1.3 nm).[46]

As the concentration of fixed ions and the water content in the membrane increases, the cluster diameter increases while the intercluster distance decreases. A feature of this situation is a marked trend to a 'collapse' of the system of hydrated clusters to form a through pore network.[40] A fraction of clusters 'merge' together, the channels connecting adjacent clusters are shortened, their diameters increase and the membrane structure becomes less regular. The transport properties of highly hydrated perfluorocarbon membranes with relatively high concentrations of fixed ionogenic groups are similar to those of the 'gel' hydrocarbon membranes. At a low content of water the properties of the two types of membranes differ appreciably in, *e.g.*, the character of dependence of the specific conductivity and diffusion permeability on the electrolyte concentration, *etc.*[47]

The cluster–network model by Gierke was subjected to criticism[13, 48, 49] because it provides no explanation for new results obtained by X-ray diffraction, Mössbauer spectroscopy, *etc.* To interpret these results, a channel model of the structure of the amorphous part of a perfluorocarbon membrane was proposed.[13] This model assumes the presence of a comb-like periodic layered system of conducting pores (channels) with a wall-to-wall distance of 3–4 nm. Tovbin, Vasyutkin and Dyakonov[48, 49] modified this model and developed a three-dimensional structural model of a perfluorinated membrane, which treats two kinds of pores, *viz.*, slit-like and cylindrical ones. The larger slit-like pores with a wall-to-wall distance of 3–5 nm are formed by close-packed polymer chains, are 10–17 nm long and 5–10 nm wide. Regular packing of polymer chains that form the 'walls' of the slit-like pores is periodically distorted by transient regions characterised by chain bending and entanglement. Such transient regions can be represented as sets of cylindrical pores formed by segments of bending polymer chains; the characteristic pore diameter and pore length are 1.5 and 2.5 nm, respectively. The role of these pores is analogous to that of the cluster-connecting channels in the Gierke model. The characteristic sizes of the structural elements in the models by Gierke and by Tovbin–Vasyutkin are in good agreement while the models themselves differ in interpretation of the cluster and channel shape.

The results obtained in a large number of experimental studies carried out to date allow definite conclusions about the structure of swollen hydrocarbon membranes. One of the pioneering works was reported by Gnusin[50] who studied inhomogeneous distribution of the concentration of ionogenic groups by microscopic observations. Similar results were also obtained by spectroscopic methods,[13, 17, 22, 51, 52] contact reference porosimetry[30–32] as well as by other methods.[34–37] Figure 3 presents the results obtained for a heterogeneous cation-exchange membrane MK-40 by contact reference porosimetry[31, 53] and mercury porosimetry.[34] The pore radius distribution curve is bimodal. Its maxima correspond to two types of pores, that is, the micropores and mesopores of radius about 10 nm and macropores of radius of the order of nearly 1000 nm. The first type of pores is localised within particles of the KU-2 cation-exchange resin employed for the preparation of the membrane, while the second type of pores represents the space between the resin and binder (polyethylene) particles.

According to Vol'fkovich *et al.*,[31] micropores (of radius 1–2 nm) and mesopores (of radius 2–10 nm) in the structure of hydrocarbon membranes involve the space between individual polymer chains and their bundles. The volume of macropores (of

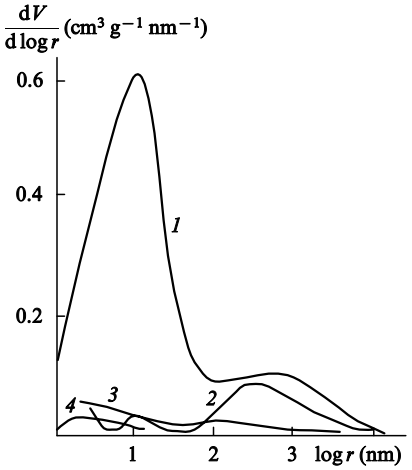


Figure 3. Pore radius distribution curves for a MK-40 membrane obtained by contact reference porosimetry (*1*),[53] mercury porosimetry (*2*),[31] (*3*)[34] and sorption technique (*4*);[34] V is the total volume of the pores of radius r.

radius exceeding 10 nm) is the space between large bundles of polymer chains and between these bundles and polyethylene binder particles. Large pores have puckered walls, the relative fraction of such pores can serve as a measure of inhomogeneity of ion exchangers. However, the total volume of large pores is much smaller (sometimes by an order of magnitude[31]) than that of the small pores, which determine the ion-exchange and sorption properties of an ion exchanger. For instance, more than 80% of pores in the MA-100 homogeneous membrane have radii less than 10 nm, while the maximum volume fraction falls to the pores of radius 4.5 nm.[31]

2. Structure of inorganic ion-exchange materials

The major distinction between inorganic systems and the polymeric systems considered above is a higher degree of structural ordering in the former material. Exchange of a particular type of ion by another one usually occurs with retention of the lattice framework. A feature of the structure of ion-exchange materials with a rigid three-dimensional framework is the high degree of retention of the type of coordination polyhedra characteristic of a certain sort of ion. Most inorganic ion-exchange materials possess cation-exchange or bifunctional properties. The latter group is mostly represented by hydrated oxides of polyvalent elements.

Among inorganic ion-exchange compounds, it is possible to identify the following classes: complex and hydrated oxides and salts of polyvalent metals. Detailed description of each class has been documented.[2, 54, 55]. In this Section we will consider the structure of some of the most widely used inorganic ion exchangers. From this point on for more systematic presentation it is convenient to divide the ion exchangers into nanomaterials, layered materials and materials with a three-dimensional framework.

A strong impetus to the development of research on nanomaterials has been noted recently. This is mainly due to the specific properties of such materials[56–60] and to advances in the synthesis, investigation and applications of fullerenes.[61–64] The geometry of small particles is to a great extent determined by the condition for a minimum surface tension energy. Therefore, a nearly spherical shape is the most typical. The developed surface of nanoparticles contains numerous uncompensated bonds, which can be stabilised upon sorption of various ions and molecules.[55] However, these species are weakly bound to the nanoparticle cage, which makes possible reversible dissociation and surface migration.[55] In combination with high surface diffusion coefficients this determines good transport properties of such materials.[60, 65, 66]

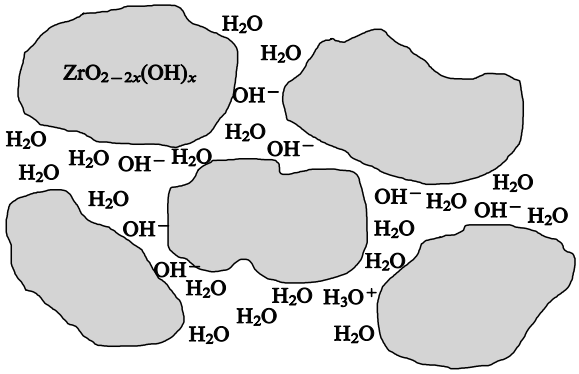


Figure 4. Schematic representation of the structure of hydrated zirconia.[54, 55]

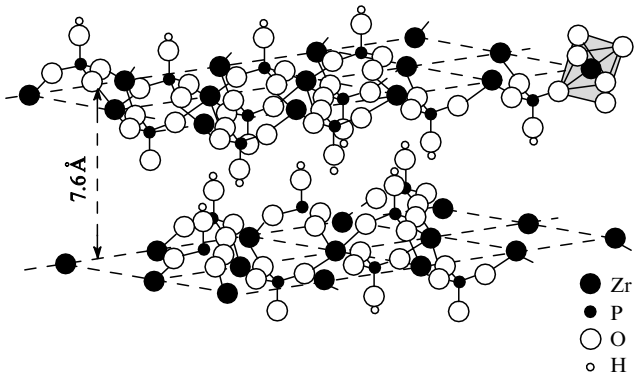


Figure 5. Crystal structure of zirconium hydrogen phosphate.[75]

This type of ion-exchange material is often called a globular hydrate.[55] Typical representatives of such materials are hydrated oxides of polyvalent metals. Ion transport in them mainly occurs within the intergrain space containing a large number of water molecules (Fig. 4). These compounds are characterised by relatively low ion-exchange capacity, which can vary by several orders of magnitude on heating or prolonged storage as a result of olation, oxolation and crystallisation processes. In some cases heat treatment at temperatures of up to 400 °C can improve the exchange properties of these compounds due to shortening of distances between hydroxyl groups and particle's surface.[67]

Structural peculiarities of amorphous hydrated oxides are due to the inhomogeneity of the bonds formed by OH groups and, as a consequence, by their ability to dissociate by acid or basic mechanisms with appreciably different dissociation constants. Therefore, the exchange capacity of hydrated oxides, which manifests itself when contacting an aqueous solution, strongly depends on the proton concentration in the solution.[54, 68] In addition, these materials can change their properties from anion-exchange to cation-exchange with an increase in the pH value of the solution. The relation between cation- and anion-exchange properties of hydrated oxides is determined primarily by the electronegativity of the structure-forming cation. For instance, double hydroxides of divalent and trivalent elements[69, 70] as well as hydrated yttrium oxide[71] are anionites. Depending on the particular conditions, hydrated zirconium and tin oxides possess both cation- and anion-exchange properties,[54] while hydrated antimony(V) oxide is a cation exchanger.[72]

Globular hydrates also comprise tungstophosphates of some monovalent metals, which possess cation-exchange properties. The number of water molecules that form a monolayer on the particle surface usually varies from 7 to 12 per formula unit. Both heteropolyanions and protons are sorbed on the surface of such compounds, which is equivalent to the deposition of acid salts in which the content of hydrogen ions can exceed 1.0 per formula unit.[73] According to NMR studies, monovalent cations on the surface of particles at room temperature are in the highly mobile state.[73, 74] It is these ions that can be exchanged with ease upon contact with aqueous solutions of salts.

The advantage of layered compounds is the high concentration of accessible sorption sites or ion exchange groups. Among this class of inorganic ion-exchange materials, hydrogen phosphates and arsenates of polyvalent elements $[MH_x(ZO_4)_2 \cdot n\,H_2O]$ (Z = P, As) are most widely used. The structure of a typical representative of this group of compounds, zirconium hydrogen phosphate, is presented in Fig. 5. Cations of small radii can migrate in the large interplanar space (interplanar spacing $d = 7-8$ Å) with ease in the direction parallel to that in which layers are aligned.[76, 77] Because of this the exchange capacity of such compounds is most often much higher than that of globular hydrates. For instance, a typical value of the ion-exchange capacity of, *e.g.*, hydrogen phosphates of tetravalent elements is 4–8 mequiv g^{-1} (see Refs 78–83). Due to the nonequivalence of hydrogen atoms and steric hindrances to arrangement of the second cation in the matrix, exchange processes in hydrogen phosphates of tetravalent elements most often involve two stages. Besides, in contrast to most polymeric membrane materials, exchange in these systems often occurs by movement of the interphase boundary, the composition of each phase being changed slightly in the course of exchange.[55, 84] Hydrogen tantalum phosphate has a somewhat lower exchange capacity (2 mequiv g^{-1}).[85] At the same time the cation mobility in this compound is much higher than that in the hydrogen phosphates of tetravalent elements.[86, 87]

Another group of layered compounds possessing ion-exchange properties comprises hydrated oxyphosphates of pentavalent metals $H_2XO_2PO_4 \cdot n\,H_2O$ (X = V, Nb, Mo). For instance, the niobium compound contains two hydroxyl groups;[88] however, only one proton in them can be replaced by a cation in the reaction with alkali.[89–92] Exchange processes in uranyl phosphate ($HUO_2PO_4 \cdot n\,H_2O$) occur similarly.[93, 94] No less important is the ability of the compounds under study to be intercalated with alkali metal cations or hydrogen, which is accompanied by reduction of a fraction of the polyvalent cations and the formation of variable-composition compounds $M_xVOPO_4 \cdot n\,H_2O$.[95–97] The latter also possess ion-exchange properties[98–100] and, in addition, high conductance, which is of great importance for the occurrence of some practically valuable transfer processes.

Layered ion exchangers comprise a giant class of clay materials built of blocks whose composition approximately corresponds to $Si_8Al_4O_{24}^{4-}$. The electroneutrality of the compound is ensured overall by the incorporation in the interplanar space of alkali or alkaline-earth metal cations or protons. A large proportion of cations located within the interplanar space can be readily exchanged. The total ion-exchange capacity of such materials can be as high as 1.5 mequiv g^{-1}. For the H-form of the materials with a nearly ideal composition the ion-exchange capacities with respect to cations and anions are approximately equal.[2, 101–103] Many layered inorganic ion exchangers are characterised by low solubility and their synthesis is, as a rule, accompanied by the formation of strongly supersaturated solutions. This leads to the formation of small particles, which are less thermodynamically stable; however, the exchange reactions on their surfaces usually occur much faster. Therefore, often researchers restrict themselves to the synthesis of materials built of rather small particles, which makes the 'boundary' between layered ion exchangers and nanomaterials diffuse. An intermediate position between the two above-mentioned classes of compounds is occupied by fibrous materials.[104, 105]

The exchange processes in the layered compounds considered above are, as a rule, accompanied by substantial changes in the interplanar spacing due to the different radii of the exchanging cations and to the change in the degree of hydration.[85] However,

not all compounds obey this regularity. In particular, practically valuable inorganic membrane materials are β-aluminates having a composition $M_{1+x}Al_{11}O_{17+x/2}$ (M^+ is a proton or the ammonium, alkali or monovalent metal cation). They also have a layered structure. A peculiar feature of their structure is that the four-layer blocks of composition $(Al_{11}O_{16})_n$ with close-packed oxygen atoms are linked by oxygen atoms of the fifth layer containing a quarter of the oxygen atoms in each of the four above-mentioned layers. Because of this the interplanar spacing varies only slightly in the course of exchange. Besides, cation exchange in such materials occurs relatively slowly at ambient temperatures. Therefore, most often the exchange processes are carried out in nitrate melts of β-aluminates at temperatures of at least 300 °C.[106–115] These compounds can be considered as a transient form between layered ion exchangers and materials with a three-dimensional framework.

Inorganic ion-exchange materials with a three-dimensional framework demonstrate the largest variety of structures. Transfer in such compounds is due to the presence of long continuous channels. Since ion transfer can occur only through migration of defects (vacancies or interstite ions), a fraction of sites 'reserved' for the mobile ions should be vacant.[6] Some examples of these compounds are provided by complex phosphates and silicates $A_xB_2(YO_4)_3$, where A is the univalent cation, B is the trivalent or tetravalent cation and Y = P or Si. Sodium-containing representatives of this type of material † are characterised by high cation mobility.[116] High cation mobility was also found in other structurally similar compounds containing protons, ammonium, lithium and some other cations (see, *e.g.*, Refs 117 and 118). The three-dimensional crystal lattice of the compounds belonging to the NASICON structural type is formed by the XO_6 octahedra (X is the trivalent or tetravalent metal) and PO_4 tetrahedra linked in such a way that three-dimensional channels extending along the crystallographic axis *c* are formed in the structure.[119] It is these channels where all the atoms of type A are located. However, if they are all occupied in $Na_4Zr_2(SiO_4)_3$, a total of 25% and 75% of sites remain vacant in $Na_3Sc_2(PO_4)_3$ and $NaZr_2(PO_4)_3$, respectively. In this connection at temperatures above the superionic phase transition temperature (320 K) a fraction of lithium atoms in the $LiZr_2(PO_4)_3$ structure cannot be located by the diffraction techniques.[119] Besides, it was found that such materials can be doped with heterovalent admixtures. For instance, it is possible to replace a fraction of phosphorus atoms by silicon, vanadium or niobium atoms.[120, 121] The largest increase in conductivity can be achieved by replacing a fraction of the cations occupying the X sites by trivalent metal cations with a simultaneous increase in the content of the alkali metal cations A (see, *e.g.*, Refs 122–125). The conductivity (cation mobility) of such systems can be several orders of magnitude higher than the conductivity of the initial phases.

Most often cation exchange in the NASICON compounds is carried out by treating the initial phase with salt melts.[126–128] Compounds with the three-dimensional framework also comprise zeolites that are widely used as sorption materials and catalysts,[102, 129–135] some complex oxides and many other inorganic materials that have been reviewed.[2, 54, 55] It should be mentioned that a large number of novel inorganic ion exchangers are synthesised and studied yearly.[136–142] High selectivity and stability of inorganic ion-exchange materials are prerequisites for the development of investigations in this area.[2, 102, 143, 144]

Recently, extensive research on the synthesis and properties of mixed ion exchangers based on inorganic matrices with chemically bound organic fragments, which contain functional groups or link individual layers and thus confine the volume of the interplanar space, has been carried out. Such ion exchangers are most often synthesised using hydrogen phosphates of tetravalent elements as matrices.[2] This allowed preparation of a large number of cation- (see Refs 145–148) and anion-exchange materials [149] possessing specific properties. Studies on the synthesis of similar materials based on other classes of compounds have also been carried out.[150]

Polymer-based composite materials with heterogeneous inorganic admixtures can be considered as a new class of ion-exchange materials. They exhibit specific physical and chemical properties and can be divided into two types, *viz*., materials with an inert and with an ion-exchange polymer matrix. In the first type of system the mobile cations are generated by the inorganic component.[151–155] Such materials are formed, *e.g.*, in the reaction of a polymer matrix with alkali metal halides or pseudohalides. The rubbery phase of the polymeric component provides a high ion mobility.[156, 157] The maximum conductivity of these composites is attained at an optimum ratio between the concentrations of the salt molecules and monomer units (this ratio is usually 0.2 to 0.4). In some cases the optimum value is much smaller.[151, 158, 159] In the initial stage of doping a sharp increase in the cation mobility is due to an increase in the concentration of charge carriers. Further increases in the cation mobility are accompanied by a substantial increase in the degree of crystallinity of the polymer and reduction of the mobility of charge carriers.[151] The effect of various microcrystalline oxides,[156, 157, 160] phosphates [161] and other heterogeneous admixtures to solid polymer electrolytes on the ion-exchange properties of the composite materials under study has been investigated.

The second type of material employs an active ion-exchange membrane capable of sorbing both cations [162–164] and anions [165] as the polymer component. The list of currently used inorganic dopants includes a variety of compounds, namely, hydrated oxides of polyvalent elements (aluminium, titanium, silicon, antimony),[162, 166, 167] heteropolyacids [163, 168, 169] and other compounds.[164] The characteristic size of the dopant species can vary from several to several hundreds of nanometres.[168] Apparently, in most cases they form islands in the membrane. For instance , a small-angle X-ray scattering study [170] revealed that the average distance between the dopant species in the Nafion–SiO_2 system is about 5 nm. The advantages of the composite membranes are mechanical strength, selectivity and the possibility of increasing the ionic conductivity of some systems, which can be as high as 10^{-3}–0.2 S cm^{-1} (see Refs 162, 165, 171).

III. Ion diffusion in solids

1. General laws

The rates of diffusion processes in various solids are substantially different. In the vast majority of compounds such processes proceed at relatively low rates; nevertheless, this does not make them less significant. For instance, very slow geochemical processes cause changes in the composition and structure of the Earth's crust.[172] Raising the temperature permits a substantial increase in the ion and molecular mobility. At high temperatures, solid-phase reactions between rather stable (at first glance) oxide phases proceed at a rather high rate.[5] Ion exchange and membrane processes are due to cation and anion diffusion.[55] The mechanism and rate of transfer in ion-exchange and membrane materials to a great extent determines the possibility of their practical use. Selective electrotransport of cations and anions through cation- and anion-exchange membranes, respectively, permits, *e.g.*, desalination of liquid mixtures.

Two mechanisms, diffusion and convection, underlie the ion transfer processes. In this review we will mostly consider the first mechanism. The rate of diffusion processes is determined by the product of the charge carrier mobility and their concentration. The first factor depends on the nature of the mobile ion and the matrix (the material in which transfer occurs).[173–175] In most inorganic compounds it is possible to select one type of ion having high mobility, which allows one to treat them as unipolar electrolytes. The highest mobility is possessed by small ions, which can

† They were called NASICON (an abbreviation of Na Super Ion CONductor).

travel with ease through faces of adjacent coordination polyhedra. At the same time, such ions must be capable of forming and cleaving chemical bonds, which implies a relatively low polarising ability. For this reason only small singly charged ions can possess a high mobility in inorganic systems at moderate temperatures (below 700–800 K). Among anions, these are only the fluoride and oxygen (at elevated temperatures) ions. Usually, cations of smaller radius also have a higher mobility. The highest ion mobility is attained for a number of compounds of monovalent metals (copper, silver and sodium).[173] Having similar radii, the first two cations offer the advantage of high polarisability of their electron shells.

The transport properties of most inorganic compounds are due to (i) the presence of vacant structural sites, in which the energy of the mobile ions is similar to the energy of the structure-forming ions, and (ii) the ratio of the cation size and the face size of the coordination polyhedron through which cation migration occurs.[174, 175] In the case of proton diffusion (small radius, $\sim 10^{-5}$ Å) the latter factor is insignificant. More important for proton transfer is the system of interatomic distances and the proton-acceptor ability of electronegative lattice-forming atoms.[176, 177]

Ion transfer in solids occurs through the migration of defects (vacancies or interstices) and the ratio of the number of defects to the number of mobile ions determines the concentration of charge carriers, which is the most important characteristic. All materials possessing high rate of ion transfer are characterised by high concentration of charged point defects.[173, 177, 178] Such an approach is applicable to a wide range of systems. For instance, water is a poor conductor first of all due to the low concentration of charge carriers (hydrated protons or hydroxide ions). The addition of acids or alkali causes the formation of defects, thus leading to a sharp increase in the conductivity of the system.[179] Analogously, the concentration of defects in the low-temperature modification of silver iodide (β-AgI) is relatively low, while it increases by several orders of magnitude in the superionic phase of this compound.[180] The concentration of defects in superionic compounds can be as high as 10^{18} cm^{-3} (see Refs 172 and 181). It is this parameter whose value determines the ability of a substance to provide fast ion transport.

The reaction of defect formation in an ionic crystal M^+X^- with Frenkel defects can be described by the following equation[182]

$$M_M + V_i = M_i^{\bullet} + V'_M , \qquad (1)$$

where M is the cation, V is the vacancy, the subscripts M and i correspond to the atom occupying the cation site and the interstice, respectively, and the superscripts (a point and a prime) respectively denote the positive and negative charge of the species with respect to the stoichiometric charge of a given lattice site. Let N_i and N_v be the mole fractions of the ion interstices and cation vacancies in the bulk of the crystal. The product of these quantities can be expressed through the equilibrium constant (K_F) or the Gibbs free energy (ΔG_F) of the reaction (1)

$$N_i N_v = CK_F = C\exp\left(-\frac{\Delta G_F}{RT}\right) , \qquad (2)$$

where C is the number of interstices per site of a regular lattice (*e.g.*, for crystals with the rock salt structure one gets $C = 2$). Since the crystal is electrically neutral, the concentrations of vacancies and interstices in the crystal have equal values. Therefore, we can write

$$N_i = N_v = (CK_F)^{1/2} = C^{1/2}\exp\left(-\frac{\Delta G_F}{2RT}\right) . \qquad (3)$$

In some materials the energies of the atoms occupying the lattice sites and the defect sites are nearly equal. In particular, the energies of the cations occupying five different sites with the coordination numbers of 5, 8 and 9 in the structure of sodium β-aluminate are similar.[183] Because of this at room temperature nearly half the sodium ions are located at sites with a higher energy, which makes the notions 'sites' and 'interstices' undefined. At the same time in the case of $NH_4Al_{11}O_{17}$ arrangement of a large NH_4^+ cation at different sites leads to a larger energy difference. Therefore, in $NH_4Al_{11}O_{17}$ almost all ammonium ions occupy the so-called Beavers–Ross sites. Clearly, in ammonium β′-aluminate, $(NH_4)_{1+x}Al_{11}O_{17+x/2}$, the excess NH_4^+ ions should occupy the interstices. This should lead to a decrease in the concentration of cation vacancies [see Eqn (3)]. However, structural studies point to a sharp increase in the number of cation vacancies with increasing concentration of interstitial ammonium ions. For instance, on average 23% of regular sites in $(NH_4)_{1.2}Al_{11}O_{17.1}$ are vacant, while the interstices are occupied by 0.43 ammonium ions per formula unit.[184] As the ammonium ion arrives at an interstice, it displaces adjacent cations from regular lattice sites to the interstices with similar energies. The formation of relatively large structural domains (clusters) characterised by the predominant population of interstices appears to be energetically favourable. It is these clusters in which the majority of excess cations is located.

The rate of ion transport can also be considerably increased by doping ionic crystals with heterovalent admixtures. Doping causes an increase in the concentration of cation vacancies or interstices. For instance, heterovalent replacement of the phosphorus or tetravalent metal atoms in high-defect solid solutions based on phases with the NASICON structure (see above) by cations of lower valence with simultaneous introduction of an excess of alkali metal results in a sharp increase in the concentration of interstitial mobile ions, which is accompanied by an increase in the ionic conductivity.[116, 122, 185] A study of a lithium-containing compound revealed the formation of clusters containing cation interstices alternating with the domains of stoichiometric composition, which is similar to β-aluminates of alkali metals. This allowed Abrahams and Bruce [186] to conclude that ion transfer in such materials involves migration of clusters containing a large number of interstices.

Replacement of silicon by phosphorus in a silicate of composition $Li_{4-x}Si_{1-x}P_xO_4$ also results in the formation of one cation vacancy in the lattice. A feature of the Li_4SiO_4–$LiAlSiO_4$ system is the formation of a continuous series of solid solutions of composition $Li_{4-3x}Al_xSiO_4$ and an individual compound $Li_5AlSi_2O_8$. West *et al.*[187] showed that individual compounds in this system exhibit the lowest conductivity. Interstitial lithium ions are the main type of defects, which determines the conductivity of the Li_4SiO_4-based solid solutions

$$Li_4SiO_4/LiAlSiO_4 \longrightarrow Li_{Li} + Li''_{Al} + 2Li_i^{\bullet} + Si_{Si} + 4O_O . \qquad (4)$$

In contrast to this, cation vacancies dominate in the solid solutions based on $LiAlSiO_4$

$$LiAlSiO_4/Li_4SiO_4 \longrightarrow Li_{Li} + Al_{Li}^{\bullet\bullet} + 2V'_{Li} + Si_{Si} + 4O_O . \qquad (5)$$

The cooperative phenomena contribute largely to transfer processes in condensed media.[188] They have a particularly strong effect on proton transfer, which always occurs by successive proton jumps from one electronegative atom to another and by rotation of proton-containing groups.[189] Water molecules located near a hydrophobic polymeric ion-exchange matrix form relatively weak hydrogen bonds and readily pass into the rotational mobility state. A rotating water molecule should be treated as a neutral spherical species rather then a dipole. Hydrogen bonds formed by this molecule are cleaved, which facilitates the mobility of the nearest neighbours. Their rotation, in turn, induces the mobility of other surrounding molecules and, finally, of the whole system. For instance, a fraction of the hydrogen bonds formed by water molecules and proton hydrates in $H_3PW_{12}O_{40}\cdot 29H_2O$, in which the anion O atoms having a low proton-acceptor ability act as proton acceptors, are very weak. The high rotational mobility of these fragments, which, in turn, function as acceptors of

protons of other H-bonds, propagates over the whole proton hydrate sublattice due to the cooperative effect. Therefore, its transition to the highly mobile state occurs at low temperatures.[190] A similar transition to the mobile state at low temperatures has been reported for layers of water molecules sorbed on the surface of some inorganic compounds.[176]

Vibrations of both solution particles and functional groups of ion exchanger induce alternating weakening of some hydrogen bonds and strengthening of some others in the system. Strengthening of hydrogen bonds brings about a decrease in the activation energy for proton transfer and accelerates proton hopping, whereas the weakening of bonds enhances the rotational mobility. These processes are separated in space, so that proton transfer acquires a cooperative character. The cooperative nature of proton transfer has also been noted for salts of polyfunctional organic acids,[191, 192] for chains of the acid $-(H_2O)_n-$ anion type [193] and for complex biomolecules.[194, 195] There are grounds to believe that the cooperative mechanism of transfer can also be involved in the case of some alkali metal cations.[196] It should be mentioned that all the systems listed above are characterised by relatively weak binding, which seems to be important for efficient cooperative processes. The higher the structural disorder and the weaker the bonds formed there, the larger the vibrational amplitude and the higher the rate of transfer. It is the weakness of bonds formed and the ease of their rearrangement that result in a large vibrational amplitude and the highest efficiency of cooperative processes.

In this connection we will return to the polymeric membrane materials considered above. A salient feature of such systems is a decrease in the ionic conductivity with a decrease in the mobility of polymer chain segments, which is accompanied by an increase in the viscosity of the polymer.[151] Taking into account this fact, Druger *et al.*[197] proposed a percolation model of transfer with allowance for correlation between cation hopping and rotation of segments of polymer chains, which induces reorientation of cation's coordination polyhedra.

Diffusion in polymeric membranes and ion-exchange materials is usually described assuming the three most probable ion transfer mechanisms, *viz*., the vacancy, relay and solvation ones.[51, 198, 199] According to the vacancy mechanism, the mobile ions migrate from one fixed (immobile) molecular group to another one. Migration occurs if at least one neighbouring group is unoccupied by an ion. The relay mechanism involves 'displacement' of an ion bound to the fixed group by a 'free' ion present in the channel. The 'displaced' ion goes to the conductive channel or displaces the next bound ion, thus maintaining the relay transmission. The third solvation mechanism deals with the motion of ions in solution and is to a great extent analogous to transfer along interstices in ionic crystals.

The first and third mechanisms can be realized simultaneously, since the counterion having escaped its potential well cannot go beyond the bulk of the ion exchanger (this corresponds to the formation of Schottky defects in crystals [200]). This relay mechanism occurs in the case of a narrow channel (pore), where the vacancy mechanism is impossible for steric considerations.[201, 202]

The depth of the potential well is determined by the energy of the coulombic interactions between hydrated ions, by the chemical interaction between the ion and the molecular group it is bound to and by the energy necessary to stretch the polymer network and thus to provide the possibility for an ion to escape.[51] For some transfer mechanisms the barrier height also depends on the energy of formation of ion vacancies and dopant ions.[200] According to quantum-mechanical calculations by Shaposhnik *et al.*,[203, 204] insertion of water molecules between the counterion and the fixed ion leads to substantial weakening of coulombic interactions between them. At the same time one should take into account the energies of the hydrogen bonds formed by water molecules with the counterions and fixed ions, which is responsible for the crucial role of hydrogen bond cleavage in ion transport. The potential barrier is determined by the elementary jump length, λ, of the diffusing ion. In ionic crystals, ion hopping from one interstice to another occurs; therefore, the λ value is determined by the lattice constant.[200] For ion-exchange materials, λ is most likely determined by the distance between corresponding molecular groups and depends on the ion-exchange capacity.[51] In conventional ion-exchange membranes the average distance between such groups is 0.5 – 1.0 nm.[13, 51] Probably, ion transfer from one fixed group to another involves a number of elementary jumps. In this case, at least in systems with a high concentration of ionic salts in channels, the role of transfer agent can be played by the mobile ions likely charged with the fixed groups (coions) or by the solvent molecules.

When estimating the self-diffusion coefficient of multiply charged ions, Shaposhnik *et al.*[203, 204] pointed out that the probability of a fluctuation, which makes possible simultaneous abstraction of an ion from several fixed groups it is bound to, is very low. Assuming that the ion escapes from the potential well in several steps, they concluded that the diffusion coefficients of the doubly charged ions must be nearly 4 times lower than those of the corresponding singly charged ions.

2. Transfer processes and interfaces

Most of the membrane and sorption processes are heterogeneous, so interfacial phenomena are of great importance in this case.[205] Frenkel [206] and Chebotin and Perfil'yev [207] pointed out that the grain boundaries and the surfaces of solid particles are sources of excess point defects, the concentration of which for ionic crystals is determined by the surface potential. Most often cations and anions are located on the surface of crystals under different conditions. Apparently, that is why cation vacancies or interstices are mainly sorbed on the surface, while defects of the opposite sign are concentrated within a thin near-surface layer. Because of this the so-called 'surface' charge appears within the Debye layer ($\sim$1 – 3 nm thick). The volume density of the 'surface' charge tends to zero with the distance from the interface to the interior of the crystal.[208 – 210] The magnitude of the charge is determined by the morphology, crystal chemistry considerations and sorption properties of the surface. The electrical double layer at the organic ion exchanger – solution interface is formed analogously.[11, 173]

The concentration of defects and the surface potential of silver chloride polycrystals were estimated by Maier [211] from the ionic conductivity of this compound. The results of calculations are in good agreement with the data obtained using independent methods. In particular, the surface potential of silver chloride and silver bromide changed from -0.1 to -0.25 eV on heating from 298 to 550 K.[212, 213] According to calculations, at room temperature the concentration of cation interstices in these compounds must be three orders of magnitude higher than in the bulk of the crystal.[212] Enhancement of the translational mobility of ions and intensification of the diffusion processes on the surfaces of crystals are due to weak binding of the surface atoms and high imperfection of the surface.[65, 66, 214]

The contribution of the surface component to transfer processes is most significant for nanomaterials, since the linear size of nanoparticles can be comparable with the thickness of the Debye layer. In this case the bulk of the particle is characterised by an increased concentration of defects and the material as such must possess an abnormally high conductivity.[215] A detailed description of ion transfer in nanomaterials can be found in reviews.[60, 216]

In the early 1970s Liang [217] discovered that the ionic conductivity of the low-temperature modification of silver iodide placed in contact with finely dispersed alumina increases by several orders of magnitude despite the fact that the latter compound did not possess conducting properties. This appeared to be of increasing interest due to the potential use of composite electrolytes in compact power sources with high capacity.[218] A number of experimental studies were carried out, aimed at increasing the ionic conductivity of silver, mercury, lithium and monovalent copper halides by doping them with finely dispersed

powder of an inert phase, for the most part finely dispersed alumina, silica and titania.[219–227] At about that time Shahi and Wagner [228, 229] and Hartwig and Weppner [230] reported an increase in the ionic conductivity of two-phase solid electrolyte mixtures ($AgI-AgBr$, $LiI-NH_4I$). In succeeding years the number of studies in this research area increased significantly.

An increase in the conductivity upon heterogeneous doping of ionic compounds is primarily determined by a substantial increase in the contribution of the surface component. Numerous attempts to explain this phenomenon have been undertaken. For instance, Stoneham *et al.*[231] postulated that the formation of the highly conducting phase is due to the presence of trace amounts of water. However, experimental data supported the assumption that an increase in the conductivity of binary systems of the $AgI-Al_2O_3$ type is first of all determined by an increase in the concentration of defects in ionic salts containing mobile ions.[220]

Suppose that the admixture (phase B) possesses the properties of a base, is chemically inert towards the ionic compound M^+X^- and forms no solid solutions with M^+X^-. It is known that two phases are in equilibrium if the chemical potentials of all components (including ions) in each phase are equal to one another. Therefore, sorption of the M^+ and X^- ions on the surface of B is possible until the ion activities are equal to those in the bulk of M^+X^-. For instance, only silver ions incapable of penetrating alumina particles are in the mobile state in the $AgI-Al_2O_3$ system; however, these ions can be efficiently sorbed at the interface. Because of this, cation vacancies are concentrated in the adjacent layer of the solid electrolyte, thus imparting a negative charge to it (Fig. 6 *a*). By analogy with the situation which takes place when a solid contacts an electrolyte solution,[232, 233] an electrical double layer is formed at the AgI/Al_2O_3 interface. A theory for this phenomenon has been developed by Maier *et al.*[208, 234–248] Defect formation can be described by the following equations:[208]

$$M_M + V_B = M_B^{\bullet} + V'_M, \tag{6}$$

$$M_B^{\bullet} + V_i = M_i^{\bullet} + V_B, \tag{7}$$

where the subscript B denotes the interfacial sorption site.

To describe the thermodynamics of interfacial processes, the functions ΔG_{vB} and ΔG_{iB} were introduced. The difference between the values of these functions at the interface and at the surface of a pure crystal equals the Gibbs free energy of migration of a metal ion from MX to the surface of the B phase. If $\Delta G_{vB} < \Delta G_{iB}$, a fraction of ions escape from the bulk and appear at the interface due to sorption. This causes a sharp increase in the concentration of vacancies within the Debye layer. The change in the concentration of cations along the normal to the interface is analogous to that shown in Fig. 6 *b*. If the phase B possesses the properties of a weak base, it does not possess the ability to sorb cations and can tear them away (adsorb anions), which leads to an increase in the concentration of interstices in the near-surface layer. In both cases for a rather strong interaction the concentration of a particular sort of defect increases, which affects the physical and chemical properties of composite systems.

Various types of interactions at solid/solid interfaces have been reported.[181, 240] In particular, the systems comprised of alumina and lithium iodide (or silver chloride, or a divalent metal fluoride) are characterised by sorption of mobile monovalent ions (Li^+, Ag^+, F^-) at the interface. As a consequence, the concentration of vacancies within the Debye layer sharply increases.[208, 243, 249] The interaction of the silver chloride surface with ammonia vapour causes an increase in the concentration of cation vacancies due to the formation of relatively strong cationic complexes at the interface.[240] In contrast to this, interaction of silver chloride or calcium fluoride with Lewis acids (BF_3 or AsF_5) results in the formation of strong surface anionic complexes. In this case the concentration of interstitial silver ions or fluoride ion vacancies within the Debye layer increases sharply.[240, 242, 244] The interaction of silver iodide with silver bromide or silver chloride also causes a substantial increase in the conductivity of the system[225, 250, 251] due to the formation of heterogeneous (AgI/AgCl) contacts, which is accompanied by an increase in the concentration of cation vacancies and interstices in the near-interface region. This kind of interphase interaction is analogous to the formation of an electrical double layer near the surface of solids immersed in electrolyte solutions.[232, 233] Sorption of oxygen atoms on the oxide surfaces also causes the formation of cation vacancies in the near-surface layer.[245]

As mentioned above, ion exchangers and membrane materials can be represented as multicomponent and multiphase systems comprised of very thin interlayers, channels or voids filled with a charged solution (micro-, meso- and macropores) and an inorganic or polymer matrix containing functional groups. Due to the interaction between the solution and matrix, spatially separated charges appear. Most often, the size of channels and pores, in which ion transfer occurs, is of the order of several nanometres (see Fig. 3). Since this size is comparable to the characteristic thickness of the Debye layer, rather intense sorption – desorption processes occur involving the overall pore system. Even in the case of contact with neat solvent the concentration of charged particles formed as a result of dissociation of functional groups or sorption of one sort of ions (solvent constituents; in the case of water these are the H^+ or OH^- groups) in the conducting channels is high. Therefore, transfer processes in these channels can be highly efficient. Besides, since changes in the concentration of charged species are most pronounced within the grain boundary Debye layer (Fig. 7), the ion distribution over the channel thickness is nonuniform. The rate of ion transport differs correspondingly.

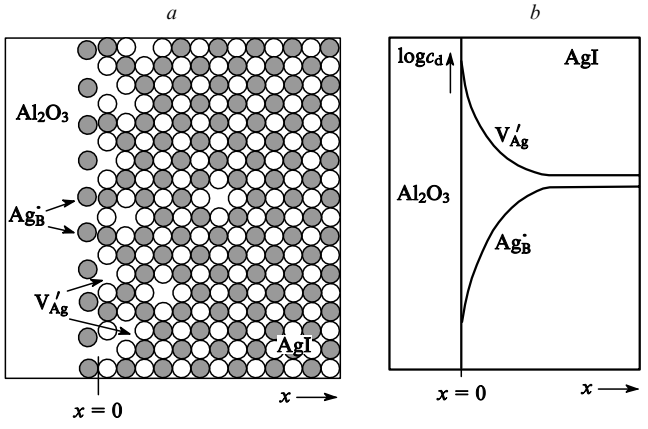


Figure 6. Scheme of defect formation at the AgI/Al_2O_3 interface (*a*) and changes in the defect concentration (c_d) within the boundary layer (*b*);[9] *x* is the distance from the surface of the Al_2O_3 particles (phase B) into the interior of the AgI particle.

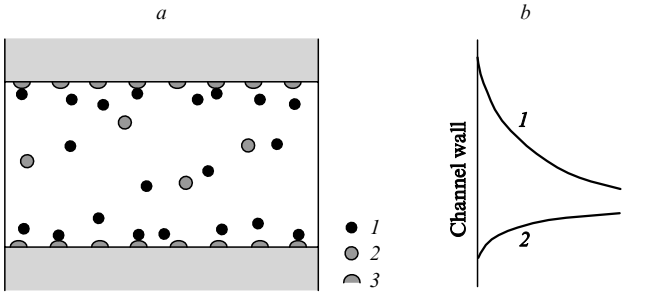


Figure 7. Counterion and coion distribution in the membrane channel (*a*) and changes in their concentrations near the channel wall (*b*); counterions (*1*), coions (*2*) and ionogenic groups (*3*).

The electric potential and ion concentration distributions in the pores of ion-exchange materials are described in the framework of the Gouy–Chapman theory and related models based on it.[252–255]

The effect of homogeneous and heterogeneous contacts on the rate of chemical transport is ambiguous. On the one hand, a considerable increase in the concentration of charge carriers within the Debye layer accelerates transfer along the boundary. On the other hand, ion transfer between two phases can be complicated because of the low concentration of charge carriers at the interface.[9, 248, 256] Besides, interfacial phenomena strongly affect the kinetics of various processes that occur involving the solid phase. Nonlinear phenomena, such as oscillating catalytic processes,[257] oscillations of the electrochemical potential on the surface of metallic electrodes,[258, 259] *etc.*, can be observed at the gas–solid and liquid–solid interfaces. Therefore, it is of importance to allow for all interactions between the membrane material and the environment in the course of ion transfer.

Let us consider transfer of the component M through an ionic compound $M^{z+}X^{y-}$ through which both ionic and electronic conduction can occur. If the driving force is weak, one can assume that the flux of the component M is proportional to the electrochemical potential gradient ($\Delta\mu_M$). Directed transfer of only one sort of ions would lead to charge separation in the membrane bulk, which requires a large expenditure of energy. Therefore, chemical transport usually involves unidirectional diffusion of differently charged ions including electrons or counterdiffusion of likely charged ions. Generally, the flux of any sort of ions can be calculated from stoichiometric ratios. For instance, the flux of metal ions is given by the Wagner equation [260]

$$J_M = -\frac{\sigma\Delta\mu_M}{(zen_M)^2}, \tag{8}$$

where σ is the ambipolar conductivity of the crystal

$$\sigma = \frac{\sigma_M\sigma_B}{\sigma_M + \sigma_B} \tag{9}$$

(σ_M and σ_B are the ionic conductivity of the material with respect to a given sort of ion and the electronic conductivity, respectively), e is the electron charge and n_M is the stoichiometric coefficient. Equation (8) is also applicable to calculations of transport through grain boundaries.[256]

Analysis of the relations listed above suggests that the rate of mass transfer is controlled by the concentration of defects possessing a lower mobility. If the limiting factor is ion transfer, chemical transport in systems with multiple boundaries characterised by an increased concentration of defects occurs at a higher rate. Acceleration of transfer involves more intense chemical transport along grain boundaries (Fig. 8 *a*).

In some cases mass transfer along grain boundaries accelerates due to the specific interaction between them. In particular, a study [261] of electrotransport of multiply charged cations across the interface between two oxide phases revealed that the properties of ceramics obtained in the synthesis of some molybdates and tungstates of divalent metals in an electric field are significantly different from the properties of ceramics obtained by sintering of oxide powders. This first of all manifests itself as a change in the adhesive properties of the interfaces between the initial reagent and product, as well as an increased concentration of diffusant on the product surface. Besides, it was shown that diffusion of molybdenum and tungsten in such systems occurs faster compared to diffusion of calcium, strontium and lead, which contradicts the commonly accepted electrotransport models. Neiman and Guseva [261] assumed that molybdenum and tungsten diffuse as constituents of 'multiparticle defect complexes' and pointed to a marked dependence of the transfer rate on the substrate porosity. Based on the aforesaid, it was concluded that MoO_3 (WO_3) interact with the reaction product as wetting agents, thus forming a thin layer of the 'surface phase', which accelerates ion transfer.

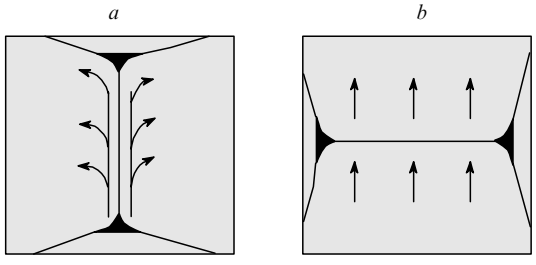


Figure 8. Schemes of mass transport along (*a*) and normal to (*b*) the interface.[256]

Studies on the synthesis of tungstates and molybdates in an electric field involving unidirectional diffusion of MoO_3 and WO_3 revealed an abnormally strong effect of the electric field on the reaction kinetics, as well as a 'non-Faraday behaviour' of the reaction and a nonmonotonic dependence of the reaction rate on the voltage applied.[262–264] Similar phenomena were also observed in studies of the interaction of (i) molybdenum and tungsten oxides with trivalent bismuth oxide [265] and vanadium and niobium oxides,[266, 267] (ii) V_2O_5 and Nb_2O_5 with rare-earth element oxides,[268] (iii) Bi_2O_3 with transition-metal oxides [269] and (iv) indium, gallium and chromium oxides with Al_2O_3 and ZrO_2.[270, 271]

Following a parallel between transfer in solids and fluids, it is appropriate to discuss the interrelation between anomalous transport properties of grain boundaries (see above) and high ionic mobility in globular hydrates whose structure was described above.

Water molecules filling the intergrain space of these compounds are bound to the surface only by weak coordination and hydrogen bonds. Therefore, water molecules are in a highly mobile state.[66, 71, 74, 189] At the same time, defect formation occurs on the surface of the hydrated particle (see above). This process is accompanied by passage of a fraction of the surface cations and anions into the newly formed solution, which, under some assumptions, can be treated as an individual phase. Ionic consituents of this phase also possess high mobility. Therefore, they can exchange with ease, as solid particles contact the surrounding real solution. (This is also the reason for the conducting properties of such compounds.[54, 71, 101]) For instance, the following process is to some extent possible:

$$SnO_{2+x}H_{2x} + y\,H_2O \rightleftharpoons SnO_{2+x}H_{2x-y}^{y-} + y\,H_3O^+, \tag{10}$$

since hydroxyl groups in $SnO_2 \cdot n\,H_2O$ can undergo dissociation by the acid mechanism.

The intergrain space of a globular hydrate is filled with a solution of composition $y\,H^+ \cdot n\,H_2O$, which is responsible for high proton conductivity of this compound (it can be as high as 3×10^{-4} S cm^{-1} at room temperature). This solution is an analogue of the charged defect layer near the surface of the oxide phase. Proton transfer in the solution filling the intergrain space of globular hydrates is similar to that occurring in aqueous solutions and proceeds by the Grotthus mechanism.[175] Related phenomena are also responsible for the conductivity of finely dispersed zirconium hydrogen phosphate (proton mobility on the surface of this compound is four orders of magnitude higher than in the bulk phase [66]) and insoluble alkali metal tungstophosphates.[74, 120]

The above-mentioned structural features of globular hydrates determine fast ion transport and the occurrence of chemical reactions involving only active surface groups. For the most part the exchanging ions migrate in the intergrain space along grain boundaries. Typical examples of chemical transport in globular hydrates are provided by numerous ion-exchange reactions occur-

ring in hydrated oxides [54, 55, 71, 101] and hydrates of heteropolyacids.[74, 120, 272]

Similar reactions are also observed in the course of chemical transport in the case of conventional polymeric membrane materials.[9, 273] Defect formation in them occurs mostly at the interface between the polymer matrix and solution filling the conducting channels.

If a transport process involves mass transfer across the interface between two crystals (Fig. 8 *b*), an additional potential difference is produced, which hinders the process. This phenomenon is analogous to the *p*–*n*-junction in semiconductors. Jamnik and Maier [256] showed that, all things being equal, diffusion through the system containing an interface oriented normal to the flow direction is substantially hindered. A large proportion of the transferred mass is concentrated at the interface between two crystals.

However, real processes involving chemical transport along the normal to the interface are much more diverse. The interphase interaction can also cause an acceleration of mass transfer in this direction. In particular, studies on the proton/alkali-metal-cation exchange reactions in titanium and zirconium hydrogen phosphates revealed a strong dependence of the reaction kinetics on pH value of the solution contacting the solid phase. The exchange rate is limited by two-dimensional counterdiffusion of the exchanging cations through the newly formed product layer.[274] The second stage of exchange is controlled by proton diffusion. Changes in the pH value in the course of the exchange reaction

$$NaHZr(PO_4)_2 \cdot 5\,H_2O + Na^+ \rightleftharpoons$$
$$\rightleftharpoons Na_2Zr(PO_4)_2 \cdot 3\,H_2O + H_3O^+ + H_2O \qquad (11)$$

cause a decrease in the calculated cation diffusion coefficient (D) in the $Na_2Zr(PO_4)_2 \cdot 3\,H_2O$ layer by three orders of magnitude and more (Fig. 9).[275, 276] For alkali solutions this is due to defect formation on the surface of crystals,[275] which to a first approximation can be described by the following quasi-chemical reactions:

$$H_H + OH^-_{aq} \rightleftharpoons V'_H + H_2O, \quad 7 < pH < 9, \qquad (12)$$

$$H_H + Na^+_{aq} + OH^-_{aq} \rightleftharpoons Na^{\bullet}_i + V'_H + H_2O, \quad 9 < pH < 11. \qquad (13)$$

The former process is predominant in weak alkaline solutions. It is accompanied by the formation of a negatively charged surface layer with a high concentration of proton vacancies. The charge of the layer can be compensated upon sorption of cations on the surface of the solid phase. At higher pH ($9 < pH < 11$), the concentration of vacancies increases and this charge compensation mechanism is no longer efficient. Therefore, insertion of sodium ions into the interstices or abstraction of anions from the surface occur simultaneously. The change in the main mechanism of defect formation is accompanied by changes in the slope of the plot of the logarithm of the diffusion coefficient *vs*. the pH value (see Fig. 9). Proton vacancies formed in the course of the process migrate into the interior of the crystal along with the oppositely charged sodium cations. In this case the concentration of proton defects in the bulk of the solid phase is related to their concentration on the surface.[76] In turn an increase in the concentration of charge carriers causes an increase in the diffusion coefficient.

At $pH < 7$, the slope of the plot of the logarithm of the diffusion coefficient *vs*. the pH value changes its sign (see Fig. 9). This means that proton interstices become the main type of defects in this range of pH values. They can be formed in the reaction

$$H^+ \text{ (solution)} \rightleftharpoons H^{\bullet}_i. \qquad (14)$$

As we approach the equilibrium position in the second stage of the H^+/Na^+ exchange on zirconium hydrogen phosphate (it is attained in the region $4 < pH < 6$ [76]), the proportion of proton interstices increases and approaches the equilibrium value when two phases, $NaHZr(PO_4)_2 \cdot 5\,H_2O$ and $Na_2Zr(PO_4)_2 \cdot 3\,H_2O$, contact each other. Thus, defect formation occurs mainly at the interface between two solid phases while the proton interstices diffuse into solution through the $Na_2Zr(PO_4)_2 \cdot 3\,H_2O$ layer.[76, 275]

Using a relation proposed [76] for nonlinear diffusion allowed a description of the defect distribution throughout the sample bulk (excluding the electrical double layer) in different stages of ion exchange (Fig. 10). Proton interstices are the main type of defects in acid media (Fig. 10 *a*). The exchange process is determined by counterdiffusion of proton interstices and sodium ions. In the case of alkali solutions the diffusion layer can be divided into two regions (Fig. 10 *b*). In the region adjacent to the unsubstituted $NaHZr(PO_4)_2 \cdot 5\,H_2O$ phase, counterdiffusion of proton interstices and sodium ions predominates, whereas counterdiffusion of proton vacancies dominates in the region near the alkali solution. In the latter case the exchange is determined by parallel diffusion of sodium ions and proton vacancies. At a point characterised by equal concentrations of proton vacancies and interstices, they annihilate and the main type of charge carriers changes.

A significant effect of anions present in solution on the kinetics of H^+/Na^+ ion exchange on zirconium hydrogen phosphate has

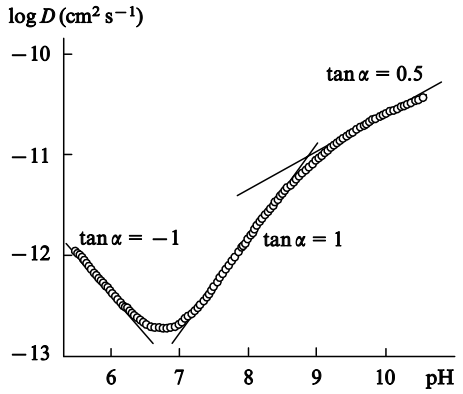


Figure 9. Calculated coefficient of cation diffusion in a $Na_2Zr(PO_4)_2 \cdot 3\,H_2O$ layer plotted *vs*. the pH value of the contacting solution.

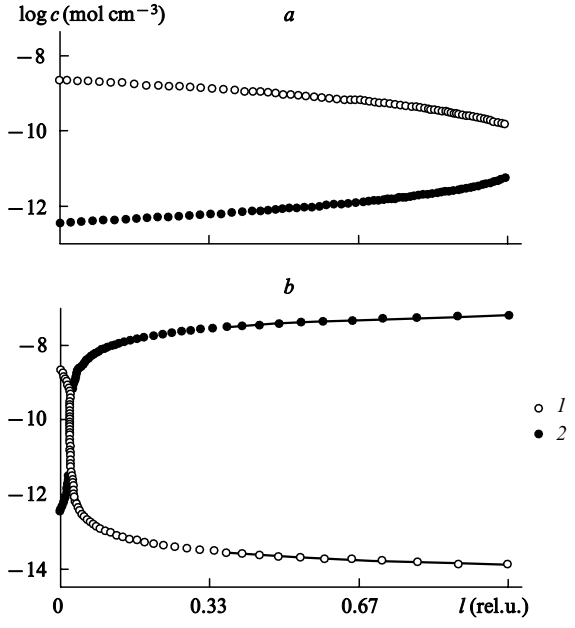


Figure 10. Change in the defect concentration (c) with the length of the diffusion layer of $Na_2Zr(PO_4)_2 \cdot 3\,H_2O$ (l) contacting a solution with pH 4 (*a*) and 11 (*b*):[76] intersticial sites (*1*) and vacancies (*2*).

been reported.[277,278] The rate of exchange increased with an increase in the sorption ability of anions on the surface of zirconium phosphate in the series $NO_3^- \approx ClO_4^- < SO_4^{2-}$ and $I^- < Br^- < Cl^-$. The increase in the rate of exchange is due to the necessity of compensating the charge of proton vacancies on the surface of the double phosphate. A possible mechanism involves desorption of phosphate ions from the surface, which becomes easy because of sorption of anions bearing a smaller charge on the free surface sites.[277,278]

These effects are much less pronounced in the case of the interaction between exchange products with different degrees of substitution. Such effects were detected in studies of the kinetics of ion exchange and ionic conductivity in the $NaHZr(PO_4)_2 \cdot n\,H_2O - H_2Zr(PO_4)_2 \cdot H_2O$ and $Na_2Zr(PO_4)_2 \cdot m\,H_2O - NaHZr.(PO_4)_2 \cdot n\,H_2O$ systems and by analysing the ^{23}Na NMR spectra.[84,87]

IV. Transport equations

1. The basic systems of equations

In deriving transport equations using the thermodynamics of nonequilibrium processes the membrane material is considered as a 'black box', since initially no information on its thermodynamic, structural and kinetic parameters is available. In the equilibrium state the electrochemical potential, $\tilde{\mu}_i$, of the ith component has a constant value at any point of the system. If the electrochemical potential gradients, $d\tilde{\mu}_i/dx$, differ from zero (for simplicity we consider a one-dimensional transfer along the normal to the membrane surface), fluxes (J_i) of the ith particles appear in the system. At small deviations from the equilibrium, the fluxes and forces inducing them are linearly related.[279–281] With allowance for the fact that the force $d\tilde{\mu}_j/dx$ exerted on particles of the j component can cause transfer of the particles of the i component (*e.g.*, electromigration of ions causes transfer of water, or electroosmosis), we get the Onsager equation

$$J_i = -\sum_j L_{ij}\frac{d\tilde{\mu}_j}{dx}. \qquad (15)$$

Determination of the phenomenological transfer coefficients, L_{ij}, is complicated by the fact that the number of these coefficients is rather large even for simple systems. For instance, for a membrane contacting a binary electrolyte solution one has to know six transfer coefficients. In addition, the local coefficients L_{ij} are functions of the local concentration of the so-called 'virtual solution'. The virtual solution was first introduced by Kedem and Katchalsky[282] and was called the 'Corresponding Solution.' This is a hypothetical solution, which is in equilibrium with a certain membrane layer.

The generalised electrochemical potential, $\tilde{\mu}_i$, in Eqn (15) can be represented as a function of the concentration (or activity a_i), electric potential φ and pressure p of the virtual solution

$$\tilde{\mu}_i = \mu_i^0 + RT\ln a_i + z_i F\varphi + \overline{V}_i p, \qquad (16)$$

where z_i is the charge, F is the Faraday number and $\overline{V}_i$ is the partial molar volume of the ions i.

To determine the local L_{ij} values characterising a thin membrane layer of thickness dx from the experimental integral values of the transfer coefficients characterising the whole membrane, the membrane must be macrohomogeneous,[283,284] *i.e.*, the L_{ij} values must be independent of the layer coordinate dx provided that each layer dx is in equilibrium with the same solution. Figure 11 presents the dependences of the L_{ij} coefficients on the concentration of the equilibrium NaCl solution obtained for a perfluorocarbon membrane Nafion-120 containing sulfonic acid groups. These coefficients were calculated[285] using the data reported by Narebska *et al.*[286,287] who carried out six experiments on measurements of the specific conductivity, apparent transport

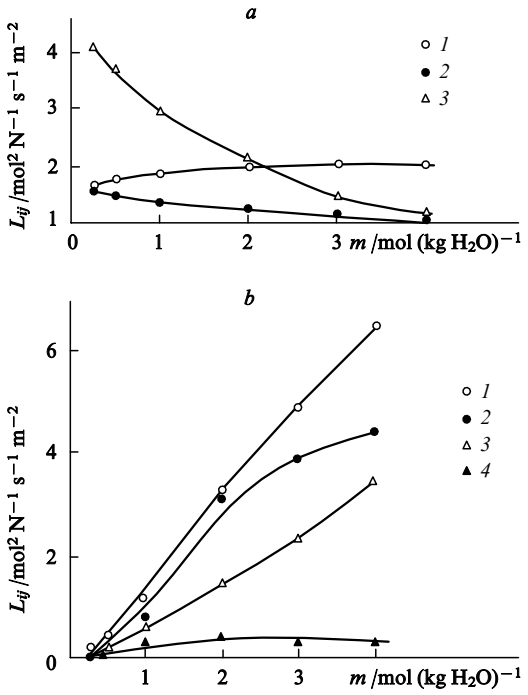


Figure 11. Phenomenological coefficients L_{ij} for a Nafion-120 membrane plotted *vs.* concentration of the equilibrium NaCl solution;[285] (*a*): $10^{10}\,L_{++}$ (*1*), $10^{9}\,L_{+w}$ (*2*), $10^{8}\,L_{ww}$ (*3*); (*b*): $10^{11}\,L_{--}$ (*1*), $10^{10}\,L_{-w}$ (*2*), $10^{11}\,L_{+-}$ (*3*), $10^{11}\,l_1$ (*4*) ($l_1 = L_{+-} - mM_wL_{-w}$, where m is the molality of the equilibrium solution, M_w is the molecular mass of water); the subscripts '+' and '−' refer to the cation and anion, respectively, and the subscript 'w' refers to water.

numbers, salt diffusion, osmotic and electroosmotic fluid flows, as well as the fluid flow due to the hydrostatic pressure drop.

The choice of fluxes (J_i) and corresponding thermodynamic forces (F_i) in the transfer equations of nonequilibrium thermodynamics is not arbitrary: if J_i and F_i are chosen correctly, the sum of their products must be equal to the dissipative function (product of the absolute temperature and the rate of entropy production per unit volume of the membrane[279–282])

$$T\frac{ds}{dt} = \sum_i J_i F_i, \qquad (17)$$

where $s = S/Ad$, S is the entropy of the adiabatic system comprised of the membrane and two adjacent solutions, A is the surface area and d is the membrane thickness. In our case the thermodynamic force has the form

$$F_i = -\frac{d\tilde{\mu}_i}{dx}.$$

It is of importance that we can choose the forces and fluxes, since this allows an appropriate description of various aspects of membrane transport phenomena. For instance, the Onsager equation, Eqn (15), is convenient for theoretical analysis since the equilibrium condition corresponds to the absence of external forces ($d\tilde{\mu}_i/dx = 0$); the well-known Nernst – Planck equation (see below) also follows from Eqn (15); finally, the contribution of coupled effects can be estimated by comparing the L_{ij} values,[286] since these coefficients are of the same dimension. At the same time the L_{ij} coefficients are related in a complex manner to the measurands (membrane conductivity, diffusion permeability, *etc.*). The use of equations similar to Eqn (15) presents some difficulties in description of transfer phenomena with a pronounced convective component.[288]

A large number of equations were proposed [288–292] in addition to the Onsager equation to allow for the coupled effects. For instance, the Stefan–Maxwell equations can be treated as an empirical generalisation of the transfer equations for ideal gases.[293] One can also derive these equations from the statistical mechanics equations in the framework of the microscopic approach. The possibility of using particle velocities instead of the flux densities and applying the pressure gradient in explicit form as the driving force also makes them convenient for the description of convective transfer.[294–296]

The so-called 'frictional' model of mass transport is based on an analogy between the motion of particles (ions, molecules) in a continuous medium and the motion of bodies in a viscous fluid. Spiegler [289] was the first who applied this theory to membranes; more recently, it was developed by other researchers.[297, 298] Other applications (transfer in ionic solutions and melts) were generalised in a monograph.[290] Studies by Meares *et al.*[297] and by Narebska *et al.*[286, 287] showed that the friction coefficients, f_{ij}, are also concentration dependent, though to a somewhat lesser extent compared to the L_{ij} coefficients.

2. The Kedem–Katchalsky system of equations

Let us analyse the Kedem–Katchalsky system of equations, which is of prime interest for a practical description of transfer through membranes.[282, 283, 299] The Kedem–Katchalsky equations are written in the form [285]

$$J_v = -L_p\left(\frac{dp}{dx} - \sigma_S RT c_s v \frac{d\ln a_\pm}{dx}\right) + \beta I, \tag{18}$$

$$J_i = -c_i L_p(1-\sigma_S)\frac{dp}{dx} - \omega\frac{d\pi}{dx} + \frac{It_i}{z_i F} = \tag{19}$$

$$= -c_i L_p(1-\sigma_S)\frac{dp}{dx} - P\frac{dc_i}{dx} + \frac{It_i}{z_i F},$$

$$\frac{d\varphi}{dx} = -\frac{I}{\kappa} - \frac{RT}{F}\left(\frac{t_+}{z_+}\frac{d\ln a_+}{dx} + \frac{t_-}{z_-}\frac{d\ln a_-}{dx} - \right. \tag{20}$$

$$\left. -\beta c_s v_i F \frac{d\ln a_\pm}{dx}\right) - \beta\frac{dp}{dx}.$$

Here J_v is the volume flux density of the solvent; J_i is the flux density of the ions i; I is the current density; c_i and c_s are the molar concentrations of the ions i and the salt in the virtual solution within the membrane, respectively; $a_\pm$ is the mean ionic activity, π and p are the osmotic and hydrostatic pressures in the virtual solution, respectively; v_i is the stoichiometric number of the ion i and φ is the electric potential.

The conducting properties of a membrane are characterised by six local transport coefficients. These are the specific conductivity, κ; diffusion permeability, P or ω; hydraulic permeability, L_p; the transport number of the counterions, t_+; electroosmotic permeability, β; and the Staverman reflection factor, σ_S, which varies from zero to unity for non-rejecting to perfect membranes, respectively.

The convenience of the practical application of Eqns (18)–(20) can be demonstrated taking Eqn (20) as an example. Here, we can distinguish with certainty between three components of the electric potential gradient, *viz.*, the ohmic (first term), diffusion (second and third terms) and the streaming potentials due to the osmotic and hydrostatic pressure drop driven transfer (fourth and fifth terms, respectively).

It should be noted that the above-mentioned systems of transfer equations including the Onsager and Kedem–Katchalsky equations are mathematically equivalent,[1] since passage from one system to another can be done by simply substituting variables.

3. The Nernst–Planck equation

The Nernst–Planck equation is most widely used in the theory of transport in membranes. This equation has a somewhat simpler form compared to the equations used in theory of nonequilibrium processes but takes into account only two main components of transfer, namely, diffusion and electromigration. It can be derived from the Onsager equation (15) assuming that the cross-coefficients are equal to zero.[289, 290] It is of interest to consider diffusion on the microscopic level by applying the random walk theory to particular ions or vacancies.[300] This permits an alternative examination of the Nernst–Planck equation.

Suppose that hopping occurs by jumps of equal length λ and that the ith ion can execute stochastic jumps in any direction irrespective of the preceding jumps, the hopping probability for any direction being constant. Then, the particle flux density along some direction is described by the Fick equation with the self-diffusion coefficient D

$$D_i = -\frac{\omega\lambda^2}{6}, \tag{21}$$

where ω is the hopping frequency, which depends on the escape frequency of the ion from the potential well (v) and on the number, n, of the nearest potential wells accessible to the ion through a single jump

$$\omega = vn; \tag{22}$$

n is the number of the nearest sites accessible to a given ion in the crystal structure or the number of fixed functional groups in an organic ion exchanger. For the vacancy mechanism of transfer n equals the number of ions in the nearest environment of a vacancy.

In the case of stochastic self-diffusion in a constant external electric field, E, directed along a particular axis x,

$$E = -\frac{d\varphi}{dx},$$

the resultant flux of the ions i through a unit of area can be defined in the same manner as in Eyring's theory of absolute reaction rates

$$J = \frac{\lambda}{2\sqrt{3}} nv\left[c_1\exp\left(-\frac{zF\Delta\varphi}{2RT}\right) - c_2\exp\left(\frac{zF\Delta\varphi}{2RT}\right)\right], \tag{23}$$

where c_1 and c_2 are the ion concentrations on the left and on the right with respect to the barrier under study. If the electric field is not too strong ($|\Delta\varphi| \ll RT/F \approx 25$ mV at room temperature), by expanding the exponents in Eqn (23) in a series and restricting ourselves to the first two terms of the expansion, we get the Nernst–Planck equation

$$J = -D\left(\frac{dc}{dx} + zc\frac{F}{RT}\frac{d\varphi}{dx}\right). \tag{24}$$

In the absence of the concentration gradient ($dc/dx = 0$) Eqn (24) takes the form

$$J = -Dzc\frac{F}{RT}\frac{d\varphi}{dx}. \tag{25}$$

Using the ion mobility u, the parameter J can be represented in the form

$$J = -cu\frac{d\varphi}{dx}. \tag{26}$$

From Eqns (25) and (26) one can get the Nernst–Einstein relationship

$$u = D\frac{zF}{RT}. \tag{27}$$

The Nernst–Planck equation is of great importance for transport theory; however, it is of limited utility. The most important conclusions reported by Buck [300] and other researchers [13, 51, 301–311] who examined limitations of this equation are as follows.

1. The microscopic approach to the derivation of the Nernst–Planck equation implies averaging over a rather large number of jumps, *i.e.*, from the molecular standpoint a membrane should be a homogeneous medium. Application of the Nernst–Planck equation to thin biomembranes, membranes with narrow (on the molecular scale) conducting channels and mosaic membranes seems to be hardly probable. The energy profile of the ion moving across a biomembrane can exhibit only 3–4 barriers;[301, 302] therefore, in this case the absolute reaction rate method is more appropriate for description of ion transport.[300, 303]

2. The Nernst–Planck equation should also not be applied at times shorter than the time necessary for averaging fluctuations of the external force exerted on an ion.[300] One of the fastest processes suitable for description by the Nernst–Planck equation is relaxation of the space charge in the electrical double layer at the interface between two electrolyte solutions or at the electrolyte solution/electrode interface.[306] The relaxation time

$$\tau = \frac{\lambda^2}{D}$$

(λ is the Debye length) is of the order of 10^{-8}–10^{-9} s for solutions with an electrolyte concentration of 10^{-2}–10^{-3} mol litre^{-1}.

3. As mentioned above, transport processes can be controlled by ion diffusion across the interface,[13, 51, 300, 304, 305] which is associated with a particular chemical reaction, rearrangement of the hydration shell, overcoming of the Coulomb barrier by multiply charged counterions, *etc*. In the last case the potential barrier can be much higher than in the bulk of the corresponding phase, while the potential jump $|\Delta\varphi|$ at the interface (overvoltage at the interface) can be comparable with the overall potential jump in the membrane system. In this case the condition

$$|\Delta\varphi| \ll \frac{RT}{\mathrm{F}},$$

necessary for the approximated expression of the exponents in Eqn (23) is broken and, hence, Eqn (24) is no longer valid.

4. Equation (24) was derived assuming a stochastic motion of ions and that each succeeding jump is independent of the preceding one. However, this assumption is often not true. Particle diffusion in crystals,[307] ion exchangers [51, 301–303, 311] and solutions [51] involves correlated successive jumps of individual species. In the case of low-concentration vacancy diffusion it is more probable for an ion to return to the initial site than to jump in another direction. Due to such a correlation the distance from the initial site travelled by the ion after n jumps will be shorter than the ion displacement caused by stochastic diffusion. In the Nernst–Planck equation the diffusion coefficient depends on the microscopic-scale transfer mechanism (self-diffusion or conduction). It seems plausible that this can be interpreted as a dependence of D on the nature of the driving force of transfer. This dependence, which is sometimes interpreted as violation of the Nernst–Einstein relationship, is taken into account using the apparent correlation coefficient

$$f = \frac{D_{i\mathrm{d}}}{D_{i\mathrm{e}}}, \qquad (28)$$

where $D_{i\mathrm{d}}$ and $D_{i\mathrm{e}}$ are the experimental diffusion coefficients determined in the self-diffusion and conduction studies, respectively. The f value primarily depends on structural features and varies for ionic crystals from 0.5 to nearly unity.[308] For the relay transfer mechanism the f value can be much less than 0.5. The f values for a number of ion exchangers have been documented.[1, 51, 308]

5. Stochastic diffusion and conduction studies revealed some differences between the interaction of an ion with the ionic atmosphere.[309, 310] Diffusion is accompanied only by the relaxation drag effect, which is due to the finite time of annihilation and creation of the ionic atmosphere (relaxation time). In the case of conduction in an external electric field an ion moves through the ionic atmosphere moving in the opposite direction rather than in a immobile medium. Therefore, the ion experiences the drug effect due to both relaxation and electrophoresis.[309, 310]

6. A significant drawback of the Nernst–Planck equation is that it does not include the parameters of water transfer and the streaming potential, which are important characteristics of baromembrane processes and electrodialysis of concentrated solutions.[311] In addition, some coupled effects due to the 'frictional' interaction between the mobile and fixed ions and molecules are also ignored. In particular, this drawback sometimes precludes the use of the Nernst–Planck equation for characterisation of ion-exchange membranes.[285]

Notwithstanding the above-mentioned limitations, the Nernst–Planck equation has found a wide field of applications. It is used for the description of transfer in liquids, solids and gels, in the bulk of the corresponding phases and at the phase boundaries. Given the activity coefficients and cross coefficients, the field of applications of this equation is extended even more. If a phase boundary can be considered as a quasi-equilibrium one, the Nernst–Planck equation is transformed into the Boltzmann and Donnan equations. As applied to electric transfer and diffusion, it is transformed into the Ohm and Fick laws, respectively. The Nernst–Planck equation describes both steady-state and non-steady-state processes including such fast phenomena as the space charge relaxation. This equation can be readily combined with other equations, which describe conjugated chemical reactions, ion and molecular association and dissociation, adsorption and the space charge formation. Combining the Nernst–Planck equation and the equations describing the hydrodynamics of a solution adjacent to the membrane permits construction of mathematical models for assessment of the role of concentration polarisation in the membrane transfer processes.

4. Generalisation of the Nernst–Planck equation

Often it is convenient to use the ion transfer equation, which is analogous to the Nernst–Planck equation but includes some coupled effects. Such an equation is obtained by substituting Eqn (20) into Eqn (19) at $\mathrm{d}p/\mathrm{d}x = 0$ assuming a linear relation between individual ion activity coefficients and the average ion activity coefficient [285]

$$J_i = -P_i \frac{\mathrm{d}c_i}{\mathrm{d}x} - \frac{z_i}{|z_i|} u_i c_i \frac{\mathrm{d}\varphi}{\mathrm{d}x}, \qquad (29)$$

where P_i is the individual local membrane permeability to diffusion of the ion i and u_i is the mobility of the ion i in the membrane. Both coefficients are explicit functions of the experimentally measurable parameters (transport numbers, conductivity, diffusion permeability and electroosmotic permeability of the membrane). This significantly simplifies the determination of the coefficients in Eqn (29). The advantage of this equation is that it implicitly (through a membrane's electroosmotic permeability) includes the effect of the streaming potential (and, hence, water transport) on the ion transfer. Finally, when using the virtual solution, there is no need to calculate the potential jumps at the membrane/solution interface and sometimes no need to determine the actual ion concentrations in the membrane.

Comparison of the Onsager and Kedem–Katchalsky equations allows one to relate the corresponding transfer coefficients.[285] It is possible to obtain six relations for six pairs of coefficients. Some of the relationships are known. For instance, one of them expresses the specific conductivity of a membrane (the

Kedem – Katchalsky coefficient) through the L_{ij} coefficients in the Onsager equation.[312–314] The following approximate equation between the Kedem – Katchalsky transport coefficients was obtained[285] neglecting the cross-coefficients that describe the interaction of coions with counterions (L_{+-}) and water (mM_wL_{-w}) in one relationship

$$P = \frac{2RT\kappa t_- t_{+ap}\gamma}{F^2 c}, \quad (30)$$

where t_{+ap} is the apparent transport number of the counterions and γ is the activity factor.[285]

Equation (30) is a generalisation of the Nernst – Einstein relationship to osmotic and electroosmotic transport of water across a membrane. To use this equation, one should know the values of all parameters. These values are hard to determine. Nevertheless, many authors[36, 285, 312–316] used and tested this equation under different conditions, mainly assuming that $t_w = 0$ and $t_{+ap} = t_+$. A rigorous study[285] of the Nafion-120, MF-4SK and MK-40 membranes revealed that the coefficient l_1

$$l_1 = L_{+-} - mM_wL_{-w}$$

has a positive value (see Fig. 11 *b*). This means that the first term (L_{+-}) describing the interaction between differently charged ions is larger than the second term (mM_wL_{-w}), which describes the interaction between coions and water. Following Kedem and Perry,[313] these membranes can be considered as hydrophobic. If $l_1 = 0$, both types of interaction are mutually cancelled out and relationship (30) should be exactly fulfilled. The case $l_1 < 0$ has been studied.[313]

Using relation (30), Eqn (29) can be transformed into a transfer equation, which is even more similar to the Nernst – Planck equation,[285]

$$J_i = L_i\left(b_i RT\frac{d\ln c_i}{dx} + z_i F\frac{d\varphi}{dx}\right), \quad (31)$$

where the L_i and b_i coefficients are explicitly expressed through t_i and κ. Here, the b_i coefficients tend to unity at c_i tending to zero and depend on the transport numbers of the ions and water.[285] The distinction between Eqn (31) and the Kedem – Katchalsky equation [Eqn (19)] is that the former ignores the interaction of coions with counterions and water. The advantage of Eqn (31) is its applicability to polyionic systems.

It should be noted that the electric potential gradient in Eqn (31) includes the streaming potential due to convective transfer driven by the hydrostatic and osmotic pressure gradients [see Eqn (20)]. Therefore, Eqn (31) implicitly takes into account the effect of osmotic volume transfer on the ion transport. In the so-called 'extended' Nernst – Planck equation these components are included in an explicit form in the convective term[11, 317–320]

$$J_i = -D_i\left(\frac{dc_i}{dx} + c_i\frac{d\ln\gamma_i}{dx} + z_i c_i\frac{F}{RT}\frac{d\varphi}{dx}\right) + c_i\vartheta, \quad (32)$$

where γ_i is the ion activity coefficient and ϑ is the linear velocity for transfer of the centre of mass of the fluid, while the concentration and electric potential refer to the whole membrane. In the calculations, ϑ is assumed to be proportional to the electric potential and hydrostatic pressure gradients;[11] it can also be found experimentally when determining the volume flux through the membrane.[320]

Equation (30) and analogous relations,[315, 316] which generalise the Nernst – Einstein equation, are used for characterisation of ion-exchange membranes;[285, 316, 321] it is more easily to calculate the transport number, t_i, from the readily measurable κ and P values than to determine it by directly measuring the ion fluxes.[322]

5. Particle diffusion kinetics of ion exchange

The kinetics of ion exchange in systems containing inorganic ion exchangers are most often studied assuming that the process is controlled by diffusion within the grain, since diffusion in solutions occurs much faster. The quantitative description of diffusion processes is complicated by the necessity of collecting a fraction of particles (crystals) of a prescribed size, which can vary over a wide range in the course of the exchange. The interdiffusion coefficients of the ions involved in the process can also change as the process is developed. This can be due to both a gradual change in the concentration of the ions of different mobility in the material under study and to the change in the characteristic size of channels and pores in the ion exchanger matrix.[55] Changes in the defect concentration in the bulk of the ion exchanger with consumption of the active component in solution can also appear to be important.[9] Nevertheless, in most cases the kinetics of exchange are described ignoring these factors.

Among the pioneering studies concerned with generalisation of the equations of transfer to objects of various geometry with inclusion of different boundary conditions was that reported by Barrer.[323] Most often, the transport phenomena occurring when an ion exchanger contacts external solution are described by the relation proposed by Boyd *et al.*[324] for diffusion in a homogeneous grain. The necessary conditions are as follows: (i) exchange occurs through the formation of a continuous series of solid solutions, *i.e.*, it does not involve any phase transitions and (ii) the grain/solution interface is in local thermodynamic equilibrium. The equation for a spherical grain has the form

$$F = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{Dt\pi^2 n^2}{R^2}\right), \quad (33)$$

where F is the fractional attainment of equilibrium, D is the interdiffusion coefficient of the ions within the grain, t is the time and R is the radius of the ion exchanger particles. The series in this equation rapidly converges for large values of F. Mention may be made that this relationship can be derived from the Fick law,[11, 325] which is a particular case of Eqn (19).

Formula (33) was used for the determination of the cation diffusion coefficients in various ion exchangers.[55] A somewhat modified relation in the differential form was proposed,[86] which includes an additional term to take into account changes in the defect formation conditions upon exchange.

In many inorganic ion exchangers the exchange processes are accompanied by changes in the phase composition. In this case the initial phase coexists with the newly formed one. The process involves a gradual movement of the interface into the interior of the grain. After solving the problem of motion of a particle in the crystal field with a periodic potential in the presence of a chemical potential gradient a relation was proposed for the determination of the diffusion coefficients from the data on the kinetics of ion exchange. In the case of two-dimensional diffusion (cylindrical grain approximation), *e.g.*, ion exchange in layered phosphates of some polyvalent metals, the relation has the form[326]

$$J = \frac{2\pi cDh\Delta\mu}{RT}\ln\frac{r_0}{r}, \quad (34)$$

where c is the concentration of the mobile ions, h is the characteristic size of the ionite particle, $\Delta\mu$ is the chemical potential difference of the exchanging ions between the surface of the crystal and the interface between the initial and newly formed phases, r is the grain radius and r_0 is the radius of the domain of the initial phase retained within the grain.

If exchange occurs through a flow of an alkali solution to crystalline α-zirconium hydrogen phosphate, the calculated interdiffusion coefficient varies by three orders of magnitude.[76] The reason is a dramatic change in the alkali concentration, which causes changes in the defect formation conditions. A relation proposed[76–84] to describe all processes occurring in the system

and the concentration distribution of various defects in the product layer is more sophisticated than Eqn (34).

It should be noted that systems with organic ion exchangers often exhibit a mixed-diffusion type of exchange. The limiting stage of such a process can change with the solution concentration, namely, transfer in dilute solutions is controlled by the diffusion through the outer diffusion layer, while transfer in concentrated solutions is controlled by intradiffusion.[11, 327–329] Nevertheless, experimental studies on ion exchange, counterdiffusion across a membrane or diffusion of one electrolyte (dialysis) provide information necessary for the determination of the diffusion coefficients [330, 331] and selectivity of ion-exchange membranes.[332] In the case of organic membranes characterised by rather high permeability with respect to water one should take into account the osmotic transfer of water and the corresponding streaming potential.[328, 329, 333]

6. Continuum models

Formal description of transfer processes involving treatment of a membrane as a 'black box' prevents the static and kinetic properties of membranes from being related to their structural features. Knowledge of such a relation is necessary to gain a better insight into the selectivity mechanism of membrane transport, dependence of the transport properties on the concentration, electric current, *etc*. This information is also necessary for chemists to obtain membranes with prescribed properties.

A large number of models relating the structural and kinetic properties of membranes have been proposed. These models can be divided into two large groups. These are the heterogeneous models, which treat a membrane as a multiphase system and characterise each phase by specific structural and kinetic parameters, and the continuum models, which concern continuous changes in the membrane properties taking into account only one phase (the membrane material can be multiphase; however, transfer in other phases is usually ignored).

The continuum models can be in turn divided into three groups:

(1) models, which treat a membrane as a single phase (charged gel); the static and kinetic parameters of the membrane (fixed ion concentration, ion diffusion coefficients, *etc*.) can continuously change with the coordinate and exhibit no explicit relation to the structural parameters;[334, 335]

(2) capillary models,[336] which are also known as the space charge models [253–255, 337–345] in which transfer is considered to be within capillary pores with charged walls;

(3) models based on percolation theory;[346–348] in this case the ion transfer is simulated by flow of a fluid through a system of voids connected by narrow channels.[13, 346]

The capillary models provide the most detailed information on the transport parameters and are based on information on the membrane structure. They were first developed to describe the electrokinetic phenomena in microcapillaries with charged walls.[254, 336] More recently,[253–255, 337–345] they were improved and adapted for the description of the membrane transfer phenomena. These models permit the inclusion of rather subtle effects, *viz*., changes in the dielectric constant with the distance from pore walls,[337] adsorption,[254, 341–343] *etc*.,[255, 344, 345] and consideration of various pore geometries (planar, cylindrical and spherical).[340]

The equation of transport in a pore schematically shown in Fig. 12 is written as the Nernst–Planck equation with the convective term (32) projected on the longitudinal (x) and normal (z) coordinates.[337, 339] The diffusion coefficient of the ions in the solution confined within the pore is usually assumed to be equal to the diffusion coefficient in free solution. The cross-sectional distribution of the local concentration, $\tilde{c}_i$, of the ions i in the pore is described by the Poisson–Boltzmann equation.[253, 339, 340] The surface density of the electric charge, q, on the pore walls is 110–440 mC m^{-2},[42, 252, 349] while the pore radius varies from 0.5 to 5 nm.[339]

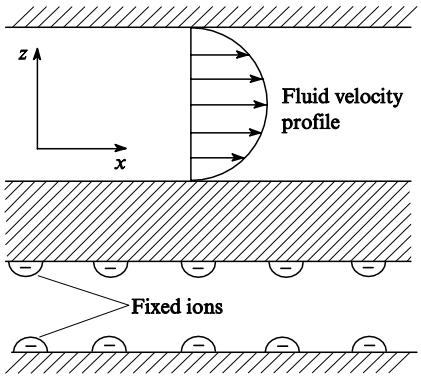


Figure 12. Schematic representation of the structure of a membrane containing parallel cylindrical pores with charged walls. The hatched area represents the insoluble polymer matrix.

The convective transfer rates, $\vartheta(r)$, were found by numerical solution to the Navier–Stokes equations.[253, 255, 337–340, 344, 345] Determination of Onsager's L_{ij} coefficients for the Nafion-120 membrane allowed [338, 350] one 'to bridge the gap' between the two approaches, irreversible thermodynamics and model description. The parameters of the model (effective pore radius, fixed ion concentration per unit volume of the solution confined inside a pore and tortuosity factor) were chosen based on the results of the porosity, exchange capacity, membrane conductivity and membrane hydraulic permeability measurements.

The percolation theory [13, 347, 348] is well adapted for the description of transfer in a system with a developed network of channels exhibiting both high and low ion transfer ability (clusters and cluster-connecting channels in perfluorinated membranes, respectively). This theory provides an explanation for the dependence of the membrane conductivity (κ) on the water content (w).[351, 352] At low water content both clusters and channels are low hydrated and their mass-transfer resistance is so high that the former virtually do not contact one another. As the water content increases, a more and more increasing number of clusters becomes connected by channels, thus forming a network penetrating throughout the whole membrane. There is a threshold water content (percolation threshold, w_0) corresponding to the insulator–conductor transition. At $w < w_0$, the membrane conductivity is zero while at $w > w_0$, it increases exponentially.[347, 348] A theoretical estimate of the exponent is 1.5 ± 0.2 for the three-dimensional system.[348] The pre-exponential factor is determined by peculiarities of the ion–ion and ion–molecule interactions and by diffusion processes between two adjacent clusters.[42, 351, 352] The percolation models for ion transfer and water transport in ion-exchange materials were developed by Timashev.[13]

7. Heterogeneous models

Analysis of the ion exchanger structure (see above) showed that the material contains more or less homogeneous regions, which are conventionally called phases.[353] One phase comprises the electrically neutral solution, which fills both macroscopic structural defects (macropores, cavities, cracks) and central parts of mesopores (clusters in perfluorinated membranes also belong to this type of defect). The second phase, which is called 'gel',[11, 354–356] is formed by an ensemble of micropores and the outer parts of mesopores containing fixed and mobile ions, water and polymer chains. Sometimes, the third (inert) phase, which is comprised of entangled hydrophobic polymer chains (the case of perfluorinated membranes) or inert binder used to improve the mechanical strength (*e.g*., heterogeneous membranes MK-40 and MA-40) is taken into consideration.

The aim of simulation of transfer in a multiphase membrane is to determine particular physicochemical properties of each phase

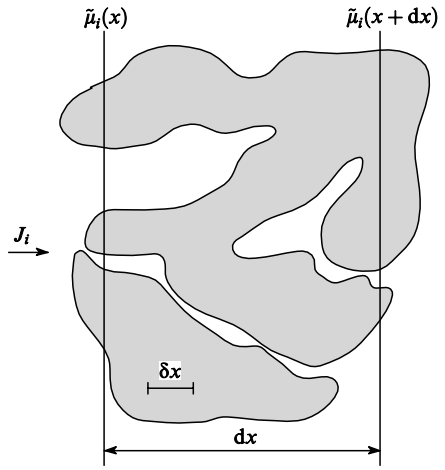


Figure 13. Schematic representation of a two-phase microheterogeneous membrane.
The shaded area is the gel phase; shown are two length scales, a microscopic (δx) and a macroscopic one (dx).

and then to obtain characteristics of the whole membrane as functions of the properties of the individual phases. Let us consider a macroscopic volume, *e.g.*, a layer containing all phases of the membrane, which are in equilibrium with one another. The thickness of this layer, dx, is small as compared to the membrane thickness (Fig. 13). In the framework of the thermodynamics of nonequilibrium processes the equations of transfer for each phase k and for the whole layer of thickness dx can be written in the form

$$J_i^{(k)} = -L_i^{(k)} \frac{\delta\tilde{\mu}_i}{\delta x}, \qquad (35)$$

$$J_i = -L_i^* \frac{d\tilde{\mu}_i}{dx},$$

where $\delta\tilde{\mu}_i$ and $d\tilde{\mu}_i$ are the changes in the electrochemical potential between points separated by the distance δx within the phase k and by the layer dx, respectively. The problem can be formulated in the following way: to determine the effective coefficient L_i^* for the membrane layer as a function of the $L_i^{(k)}$ coefficients, which characterise individual phases, and the geometric parameters, which describe the shape and mutual position of the phases.

Search for the functions relating the effective conductivity to the corresponding characteristics of individual phases for various transfer phenomena (conduction, diffusion, heat transfer, *etc.*) has been ongoing for many years. As long ago as 1873 Maxwell [357] reported a solution to the problem of conduction in a conducting medium containing widely separated spheres whose specific conductivity differs from that of the medium. Studies by Rayleigh,[358] Landau and Lifshitz,[359] Bier, Lichnecker and Roter (see references cited in Ref. 360) and other researchers [361–366] who contributed largely to the solution to this problem should be pointed out. The results obtained were generalised in a hypothesis called the 'generalised conduction principle',[361] according to which the function relating L_i^* to $L_i^{(k)}$ is independent of the nature of both the force exerted on the heterogeneous system and the substance transferred.

The structure of ion-exchange membranes was described using various approaches,[11, 354–356, 363] which were analysed in some reviews.[9, 362, 364] In the early stage, heterogeneous structural–kinetic models for the description of the shape and mutual arrangement of phases included a rather large number of parameters, which made their use difficult. Gnusin and Grebenyuk [354] proposed the so-called three-channel model for charge transfer in inhomogeneous membranes. They distinguished three types of conducting channels: gel segments, gel-connecting channels and the mixed channel. The model permitted a correct description of the concentration dependence of a membrane's specific conductivity; however, it required knowledge of three independent geometric parameters. More recently, Gnusin *et al.*[365] developed a two-parameter procedure for description of the geometry of the system. Yet another stride taken towards the development of heterogeneous models was the passage from a particular type of force (electric or diffusion) exerted on the system to the generalised force in the form of the electrochemical potential gradient.[366] A so-called 'microheterogeneous model', which included both improvements mentioned above, was developed.[36, 366–369]

The basic principles of the 'heterogeneous interstitial solution' model [370] are similar to those of the microheterogeneous model described below. For simplicity, let the ion exchanger be a two-phase system comprised of the gel phase and the gel-connecting channels filled with the equilibrium solution, the volume fractions of the phases being f_1 and f_2, respectively. By writing the equation of transfer for each phase and using the continuity condition for the electrochemical potential at the interface one can obtain the equation in the framework of the microheterogeneous model [36, 366]

$$L_i = \left[f_1 \overline{L}_i^{\alpha} + f_2 (L_i^*)\right]^{1/\alpha}, \qquad (36)$$

where $\overline{L}_i$ and L_i^* correspond to the gel phase and to the solution phase, respectively, and α is the structural parameter. The relation (36) is a generalisation of particular expressions obtained for two limiting cases, *viz.*, parallel ($\alpha = 1$) and series ($\alpha = -1$) arrangement of the phases with respect to the transfer direction; in intermediate situations, the α value lies in the range $-1 < \alpha < 1$.[366] The L_i and $\overline{L}_i$ parameters can be expressed through ion diffusion coefficients in the corresponding phases, D_i and $\overline{D}_i$

$$L_i = \frac{D_i c_i}{RT},$$

$$\overline{L}_i = \frac{\overline{D}_i \bar{c}_i}{RT},$$

while the ion concentrations in the gel phase, $\bar{c}_i$, can be found from the corresponding concentrations in the solution phase, c_i, using the Donnan equation.

The diffusion coefficients in the interstitial solution are assumed to be equal to those in free solution. The model permits calculations of the ion concentrations in the gel phase, $\bar{c}_i$, and the effective membrane conductivities, L_i^*, as functions of the electrolyte concentration in the interstitial solution.

The advantage of the model is the possibility of description of the static and transport properties of a membrane using one set of structural and kinetic parameters (see above). In this connection it is of interest to calculate the d.c. and a.c. specific conductivities of the membrane (κ_d and κ_a, respectively). The relation between κ_d and κ_a was studied by Gnusin *et al.*[366, 367] who derived and experimentally tested the following approximate formula

$$\kappa_d = \bar{\kappa}^{f_1} (\kappa^* t_i)^{f_2} = \kappa_a t_i^{f_2},$$

where $\bar{\kappa}$ and κ^* are the specific conductivities of the gel phase and the interstitial solution, respectively, and t_i is the transport number of the ions i in solution. The κ_a values can be calculated using an approximate relationship, which is valid at $\alpha \to 0$,[366]

$$\kappa_a = \bar{\kappa}^{f_1} (\kappa^*)^{f_2}, \qquad (37)$$

according to which the $\log \kappa_a - \log \kappa^*$ curve must be linear with a slope of f_2. Indeed, as can be seen in Fig. 14, Eqn (37) permits the correct description of the experimental data. The f_2 values calculated using Eqn (37) and those determined in the electrolyte sorption, contact reference porosimetry and differential scanning calorimetry studies have been compared.[34–36] The similar values of this parameter determined by independent methods indicate

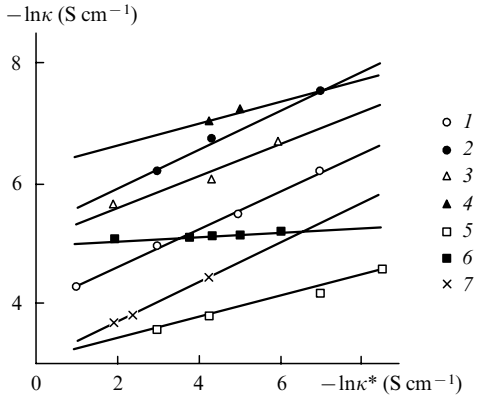


Figure 14. Plot of the a.c. specific conductivity of ion-exchange membranes *vs*. the specific conductivity of solution.[36]
Membrane in solution: C-60/65 in HCl (*1*); Amberplex C-1 in NaCl (*2*) and KCl (*3*); Amberplex A-1 in NaCl (*4*); AMF C-103 in NaCl (*5*); MF-4SK in NaCl (*6*) and Nepton CR-61 in KCl (*7*).

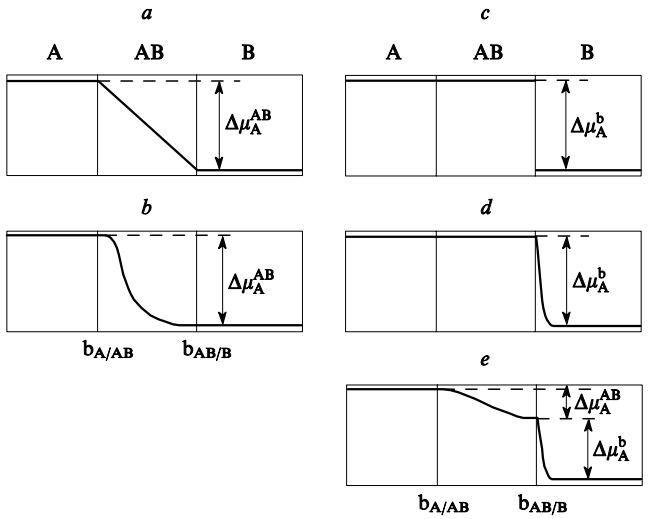


Figure 15. Change in the chemical potential along the normal to the interface for solid-phase reactions.[9]
The reaction is controlled by: diffusion, D = const (*a*); diffusion, D = var (*b*); mass transfer through the interface (*c*); relaxation processes in near-surface layer (*d*); change in the chemical potential due to diffusion and relaxation processes (*e*).

that the microheterogeneous model correctly describes the structure of ion-exchange membranes and that the electrically neutral solution characterised by the volume fraction f_2 does exist within the membrane. Equation (37) and the microheterogeneous model has been used by many researchers for estimation of the degree of heterogeneity of organic ion-exchange membranes.[371–373]

Summing up, mention should be made that capillary and microheterogeneous models considered above use all transport equations and all relations between the transport coefficients, which were obtained in the framework of the thermodynamics of nonequilibrium processes. Additional parameters, which depend on the membrane structure, allow one to relate the transfer coefficients to the structural–kinetic parameters of the membrane and to the concentration of the equilibrium solution.

V. Limiting stages of transfer and diffusion layers

1. Change in the electrochemical potential and limiting stages of transfer

As mentioned above, directed diffusion in membrane materials is driven by the electrochemical potential gradient produced in the system for various reasons.

A peculiar feature of heterogeneous processes is a nonuniform change in the electrochemical potential gradient along the normal to the interfaces. The systems comprised of membrane or ion-exchange materials usually have a multilayer structure. Often, membranes themselves contain some layers; *e.g.*, bipolar organic membranes[374] and membranes with a modified surface layer[375,376] comprise two layers. In any case the membrane is surrounded by two diffusion layers of the solution (see below). Under intense current regimes in solution a macrosopic space charge appears near the membrane surface.[377,378] This charge can also be considered as a layer which resists mass transfer. The electrochemical potential changes differently on going through different layers of the system; the layers characterised by maximum potential jump exhibit the highest mass-transfer resistance.

Let us consider the interaction between the compounds A and B, which involves the formation of a new phase AB due to the diffusion of A across the product layer and the movement of the AB/B interface. Different types of changes in the chemical potential of the component A, $\Delta\mu_A$, in this system are shown in Fig. 15. If a reaction is controlled by the diffusion across the product layer, it is this layer that contributes predominantly to the change, $\Delta\mu_A$. If the coefficient of diffusion through this layer can be considered constant, the chemical potential of a quasi-stationary process decreases uniformly, since the ion fluxes through any cross-section must be equal (Fig. 15 *a*). However, more often (taking into account the phenomena considered above) the interaction between the product and the initial components causes an increase in the defect concentrations at the A/AB and AB/B interfaces. This violates a uniform decrease in the chemical potential. If differently charged defects (*e.g.*, cation interstices and vacancies, as in the ion-exchange process described above) are generated at the oppositely lying interfaces, the chemical potential changes to the greatest extent at a point corresponding to the minimum value of the overall diffusion coefficient with respect to both types of defects (Fig. 15 *b*).[76]

Even higher chemical potential gradients can be achieved for the reactions controlled by interfacial processes (Fig. 15 *c*,*d*). The rates of such processes are determined by the surface area of the interphase boundary and by the properties of the phases. It is commonly accepted that the surface processes controlling the rates of chemical reactions can proceed by two main mechanisms, that is, activated diffusion across the interface and relaxation resulting in a structural rearrangement. The chemical potential decreases primarily at the moving interface in the former case (see Fig. 15 *c*) and in a narrow near-interface region within a certain initial component in the latter case (see Fig. 15 *d*). Real systems usually exhibit a combination of the case shown in Fig. 15 *c* or Fig. 15 *d* with a decrease in the chemical potential within the product layer (Fig. 15 *e*). It was concluded[379] that high activation energies for ion transfer across the interface are hardly probable, since the interface has an increased energy and the diffusion processes in the near-interface region are accelerated. Therefore, in the text below emphasis is placed on the relaxation processes in the region adjacent to the reaction product.

An increase in the chemical potential difference for the ions A at the AB/B interface causes acceleration of their transport across the interface and the formation of a supersaturated solution of A in the near-interface region of the phase B. Passage of the solution to the AB region requires its ordering and a change in the geometry of the environment. In particular, the formation of a large number of linear dislocations and point defects at the interface in the case of interaction between the crystalline phases AB and B and a solid solution is due to different lattice parameters of these phases. For the reasons described above transformation of the A–B solid solution into a chemical compound is accompanied by transfer of the ions A and B within the solution. Such a process inevitably requires the overcoming of some activation

barriers and a time delay (induction period). According to Schmalzried and Janek,[379] the average time taken to transfer the silver ions across the α-AgI/β-Ag_2S interface is five orders of magnitude shorter than the corresponding times of the individual phases. The structural rearrangement region can be as thick as ~ 10 nm,[379] which exceeds the thickness of the Debye layer and corresponds to several tens of crystallographic planes.

The flux of the ions A across the AB/B interface (J_A) is given by the Nernst–Planck equation. The J_A value can be determined from electrochemical experiments (*e.g.*, 2.3×10^{-5} mol cm^2 s^{-1} for the α-AgI/β-Ag_2S interface at 260 °C[380]). Mass-transfer resistance at the interface can be due to some other processes, namely, a chemical reaction (*e.g.*, complexation), rearrangement within the hydration shell, overcoming of the Coulomb barrier by multiply charged counterions, *etc.*[13, 51]

As the reaction passes, the thickness of the product layer (L_{AB}) increases, which causes an increase in the diffusion resistance of the AB layer and in the total change in the chemical potential within this layer ($\Delta\mu_A^{AB}$). The overall change in the chemical potential of the system equals the Gibbs free energy of the reaction (ΔG_{AB}); therefore, a change in ΔG_{AB} is accompanied by a change in the potential difference at the AB/A interface (see Fig. 15*e*)

$$\Delta\mu_A^b = \Delta G_{AB} - \Delta\mu_A^{AB}.$$

Since we deal with a quasi-stationary process, the fluxes of A through the interface and through the AB layer must be equal to each other

$$J_A = -\frac{J_A^0 \Delta\mu_A^b}{RT} = -\frac{D_A^{AB} c_A^{AB} \Delta\mu_A^{AB}}{RTL_{AB}}, \quad (38)$$

where D_A^{AB} and c_A^{AB} is the diffusion coefficient and concentration of A in the AB layer, respectively. From this one can readily obtain the condition for equality of $\Delta\mu_A^b$ and $\Delta\mu_A^{AB}$, which corresponds to the change in the limiting stage of the reaction from interfacial relaxation to diffusion in the AB layer. This situation occurs as the AB product layer reaches some characteristic thickness at which the dependence of the mass of the product on the duration of the reaction changes from linear to parabolic. The characteristic thickness of this layer for, *e.g.*, the formation of spinels, is of the order of 1 μm,[380] while the time taken to change the type of the limiting stage is of the order of several minutes.[381]

Ion transfer in a complex multilayer system is controlled by those layers for which the electrochemical potential jump is comparable to the overall change in the electrochemical potential in the system. If the potential jump for a particular layer is small compared to the overall change in the potential, the electrochemical potentials at the left and right boundaries of the layer can be considered approximately equal. Then to a first approximation the boundaries can be treated as being in quasi-equilibrium with each other. This assumption essentially simplifies the determination of the fluxes of the solution components through the membrane. Usually the surface layers of a membrane are assumed to be in local thermodynamic equilibrium with the surface layers of the solution, which allows one to relate the boundary concentrations in the membrane to the boundary concentrations in the solution by the Donnan relations.[1, 11, 327] Timashev and co-workers[13, 304, 305] examined nonequilibrium boundary conditions applicable to, *e.g.*, membranes with modified surface layers.

2. Diffusion layers

In some cases the rate of transfer across a membrane is controlled by mass delivery to (or rejection from) the membrane surface from the bulk of the solution through the boundary layer adjacent to the membrane (this layer is called the diffusion layer).

The concept of the diffusion layer was proposed by Nernst[382] who studied the dissolution of solids and assumed that the rate of the process is limited by the diffusion across the non-stirring boundary layer of the fluid of thickness δ

$$J = -\frac{D(c_0 - c_s)}{\delta}, \quad (39)$$

where D is the diffusion coefficient of the solute, c_0 is the concentration in the stirring solution and c_s is the concentration of the substance at the interface with the solid.

Levich[383] reported a consistent interpretation of the concept of the diffusion layer in the framework of his theory of convective diffusion. According to this theory, the flux density vector of a substance in a fluid has a diffusive and convective components

$$\vec{J} = -D\mathrm{grad}c + c\vec{v}, \quad (40)$$

where c is the concentration of the substance and $\vec{v}$ is the velocity of the centre of mass.

Convective transfer within the diffusion layer is possible but tends to zero as the solid surface is approached. Nernst's conception of the boundary layer, in which mass transfer occurs by diffusion only, can be considered as a convenient idealisation. The thickness of the diffusion layer is determined by the coordinate of the intersection point of the tangents to the concentration profiles at the solid surface and in the bulk of the stirring solution.

The following expression was derived for calculating the thickness of the diffusion layer in the case of a laminar flow of a fluid in a channel formed by two plane-parallel plates

$$\delta = 1.02\left(\frac{yDh}{\bar{v}}\right)^{1/3}, \quad (41)$$

where y is the longitudinal coordinate measured from the inlet of the channel, h is the distance between the plates and $\bar{v}$ is the average fluid flow velocity. Numerical test calculations carried out in the framework of the convective-diffusion model of electrodialysis[384, 385] showed[385] that this formula is valid for relatively short channels ($y \leqslant 0.02\bar{v}h^2/D$). In this case the thicknesses of the diffusion layers adjacent to membranes are small compared to the intermembrane distance h (Fig. 16). On further increase in the channel length the horizontal plateau in the concentration profile becomes diffuse, the diffusion region fills the entire channel, and the concept of the diffusion boundary layer loses its meaning. According to numerical calculations,[385, 386] the thickness of the diffusion layer formally determined from the intersection point of the tangents is nearly one third of the intermembrane distance.

Experimental studies on the concentration distributions in the desalination compartments of electrodialysis cells have been reported.[387–389] When the solution flow hits barriers present in

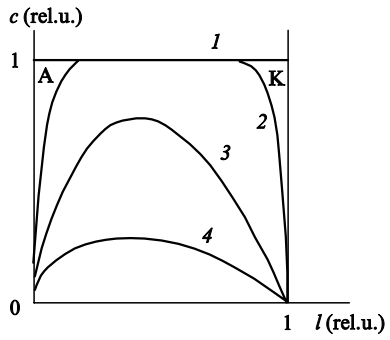


Figure 16. NaCl-Concentration profile in the desalination channel [combination of an anion-exchange (A) and a cation-exchange (K) membrane] of an electrodialysis apparatus at different values of dimensionless longitudinal coordinate $Y = yD/(\bar{v}h^2)$. Calculated using the convective-diffusion model;[384] Y: 0 (*1*), 0.001 (*2*), 0.05 (*3*) and 0.2 (*4*).

the channel (separator, ionite granules), the diffusion layer is partially interrupted; its local thickness varies periodically.[386, 390]

In the case of ion exchange and electrolyte diffusion across a membrane the concentration profiles are formed in both the ion-exchange material and the adjacent diffusion layers. The shape of the profiles depends on the dimensionless relative diffusion permeability of the membrane, p (Fig. 17),[1, 391]

$$p = \frac{Pc^{I}\delta}{Dd},$$

where P is the diffusion permeability of the membrane, D is the electrolyte diffusion coefficient in the solution and d is the membrane thickness. At small p, the concentration and, hence, the electrochemical potential change primarily within the membrane (particle diffusion kinetics), while at large p this occurs within the diffusion layers of the solution (film diffusion kinetics). For organic membranes, the P/D ratio is of the order of $10^{-1}-10^{-2}$, while the δ/d ratio varies from 0.1 to 1; hence one gets $p \approx 10^{-3}-10^{-1}$. For most inorganic membranes $p < 10^{-2}$ and the change in the concentration within the diffusion layers can be neglected. The role of the parameter p is analogous to the role of the Biot or Helfferich criteria [11, 327] used in ion exchange theory; sometimes, the reciprocal of p, or the relative electrodiffusion resistance of the membrane, is used.[1, 391]

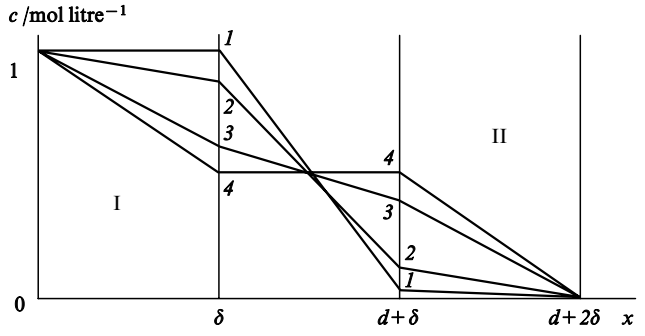


Figure 17. Concentration profiles obtained for the virtual solution in the membrane and in two diffusion layers (I and II) in the case of a binary electrolyte diffusion ($I = 0$).
Calculated using the microheterogeneous model for the MK-40–NaCl system, $\delta^{I} = \delta^{II} = \delta$; $p = 0.01$ (*1*), 0.1 (*2*), 1 (*3*) and 10 (*4*); $c^{I} = 1$ mol litre^{-1}; $c^{II} = 0$.[368]

However, a complete analogy between the electrolyte diffusion and ion exchange is possible only at a zero current. Due to the difference between the transport numbers of ions in the solution and in the membrane the flow of a current of density I causes desalination of the solution layer adjacent to one membrane surface (a diffusion layer depleted in electrolyte is formed), while the solution in the layer adjacent to the other membrane surface is concentrated.[11] As the potential jump increases, the electrolyte concentration at the depleted-diffusion-layer/membrane interface becomes much lower than in the bulk of the solution and the current density reaches the limiting value, I_{lim}. In an ideal system characterised by a constant thickness of the diffusion layer and local electroneutrality the current density must not exceed the I_{lim} value. However, in real systems, especially in dilute solutions, the current density can be several tens of times higher than I_{lim}.[392–397] This is due to a number of phenomena [394–405] involving electrodiffusion transport at high voltages: generation of the H^+ and OH^- ions upon irreversible splitting of water at the membrane/solution interface;[394] coupled convection due to the concentration and (or) temperature gradients (gravitational convection) [394–397] and the space charge density gradient (electroconvection);[398–404] and the 'exaltation' effect.[394, 405] It should be noted that experimental and theoretical investigations of these phenomena are of importance for understanding and optimising the electrodialysis process under intense current regimes.[394, 402]

The limiting current density is inversely proportional to the thickness of the diffusion layer δ.[1, 11] This dependence is often used to determine the δ value from the limiting current density at the membrane surface [406, 407] or from the limiting flux of a particular component.[408] For dilute solutions the accompanying effects mentioned above cause a significant distortion of the shape of the current-*vs*.-voltage curve, thus hampering a correct determination of the limiting current and δ value.[394, 406, 409] A method involving the use of an auxiliary electrode system to eliminate this problem has been developed.[406]

3. Limiting stages and mathematical description of multistage transfer

Determination of the limiting stages of a transfer process is of considerable importance for an understanding and practical implementation of the process. However, this is a complicated problem. As mentioned above, ion transfer across a membrane is generally a mixed-diffusion process,[306, 327, 391] *i.e*., the resultant rate of transfer is determined by transport through both the membrane and the diffusion layers of the solution. As the current strength increases, the role of the depleted diffusion layer in controlling the kinetics of the ion transfer process becomes increasingly important irrespective of the p value and in the limiting case it is transfer through this layer that is the limiting stage of the process. Taking into account this fact, it is possible to explain many experimentally observed regularities of ion transport in membrane systems. For instance, the loss of transport selectivity of a particular type of the competing counterions across the membrane is due to the change from particle diffusion (or mixed-diffusion) kinetics at low currents to film diffusion kinetics at currents close to the limiting current.[391, 410, 411] Even in the presence of a specially modified surface layer,[375] which resists the transfer of two competing counterions in different manners, the transfer permselectivity can be significantly improved only at currents lower than the limiting current.[410, 412]

Ion transfer is often complicated by the occurrence of chemical reactions, *e.g*., water splitting at the interface between two layers of a bipolar membrane [392, 393, 413–417] or near the membrane/solution interface.[392–394, 414–421] This is possible if currents close to or exceeding the limiting current flow in the system, in the case of association or dissociation of weak electrolyte ions and molecules (amino acids) accompanying the so-called facilitated transfer [422–426] or in the case of electrodialysis of natural water (carbonates, phosphates).[427–430] Water splitting in aqueous solutions is a slow process with a rate constant of 2×10^{-5} s^{-1} (see Ref. 392) and can therefore be the limiting stage of transfer in membrane systems. However, the mechanism of this reaction is rather complicated. In the membrane's bulk within a thin boundary layer 1–10 nm thick the reaction is accelerated, being catalysed by some functional groups (secondary and tertiary amines, weak acid carboxylic groups), heavy metal ions and by the electric field gradient of the electrical double layer,[392, 414–417, 431, 432] which can be as high as 5×10^{8} V m^{-1} (see Ref. 392). As a result, the reaction rate can increase by nearly five orders of magnitude. In some cases this is the desired effect (in, *e.g*., production of acids and alkali from salts using bipolar membranes [374]), whereas in other cases this significantly complicates the technological process (in, *e.g*., desalination of solutions by electrodialysis [356, 433]). The hydrocarbonate ions in the membrane can also catalyse water splitting, thus increasing the generation rate of the H^+ and OH^- ions (see Ref. 429). At the same time dissociation of some weak electrolyte anions at the membrane boundary can to some extent control the rate of electrodialysis.[356, 433]

Thus, studies of transport inside a membrane only are insufficient for understanding the transfer processes in membrane systems. Transfer across the diffusion layers and interface (more

exactly, matching these processes and transport within the membrane) strongly affects the behaviour of the whole system. The three-layer mathematical models of transfer in membrane systems [1, 369, 391, 410, 411, 434–441] give an adequate insight into the processes, since transfer is considered both within the membrane and in two diffusion layers adjacent to the membrane. The three-layer mixed-diffusion model was first proposed by Wills and Lightfoot [434] for electrodiffusion of a binary electrolyte. Electrodiffusion of binary and ternary electrolytes across a homogeneous [391, 434–437] and a microheterogeneous membrane [369, 411] has been studied. Zholkovsky [436] and Gnusin [421] included transfer of the H^+ and OH^- ions appearing due to splitting of water at the membrane/solution interface. The contribution of electroosmotic ion transfer has been reported.[319] Using a specific numerical procedure, Manzanares *et al.*[306] included violation of the electroneutrality conditions within the diffusion layers and the membrane. The role of the modified surface layer was elucidated,[410] the bi-ionic potential was studied [328, 329] and facilitated diffusion of amino acids across the membrane was investigated.[422–425]

The authors of all the studies mentioned above used similar formulations of the mathematical problems, the differences being due to the desire for taking into account a particular additional effect. Transfer across both diffusion layers ($0 \leqslant x < \delta^{I}$ and $d+\delta^{I} < x \leqslant d+\delta^{I}+\delta^{II}$) and the membrane ($\delta^{I} \leqslant x \leqslant d+\delta^{I}$) (see Fig. 17) is described by the Nernst–Planck equations [306, 391, 439] under local electroneutrality. It is also assumed that the membrane boundaries are in local thermodynamic equilibrium and that the continuity conditions hold for the electrochemical potential and fluxes. The concentrations of all types of the ions i at the outer boundaries of the diffusion layers (c_i^{I} and c_i^{II}) are specified, while the current density is considered known. In this case the problem posed is a boundary-value problem for a three-layer domain. Solving this problem involves determination of the fluxes, concentration and potentials as functions of the coordinate x.

A general analytical solution to the problem for a single-layer domain was proposed by Schlögl.[292] The system under study was also divided into three domains (see Fig. 17) and the corresponding solutions were matched.[391, 435, 439] Garrido *et al.*[319] and Karlin [437] proposed numerical methods suitable for the steady-state and non-steady-state cases. Sistat and Pourcelly [439] reported an analytical solution to the problem for a binary electrolyte using the Lambert function. Lebedev *et al.*[391, 411, 440, 441] modified the known 'shooting' method [442, 443] in order to adapt it to multilayer domains. More detailed reviews of the methods for solving this type of problem can be found in Refs 411 and 438 and in the monograph.[1]

The use of the local electroneutrality condition makes the models used rather accurate provided that the current density is lower than I_{lim}. However, many practically important processes (*e.g.*, deionisation of water by electrodialysis [356, 444] or operation of bipolar membranes [374]) require intense current regimes when the current density exceeds I_{lim}. Levich [445] considered the problem of ion transfer across the electrode/solution interface and showed that the concentration of the electrically neutral electrolyte solution near the electrode surface (c_s) varies at low currents. Simultaneously, the thickness of the diffuse part of the electrical double layer changes; however, the Boltzmann equilibrium distribution of the ion concentrations in this part is retained. The thickness of the electrical double layer is inversely proportional to $\sqrt{c_s}$ and, therefore, increases with a decrease in c_s. An analogous conclusion was also drawn by the authors of Refs 446 and 447 who extended the range of the current strengths to $I = I_{lim}$. Rubinstein and Shtilman [398] first obtained a numerical solution to the Nernst–Planck–Poisson equations for the overlimiting current flowing across the diffusion layer adjacent to the ion-exchange membrane. They showed that at $I > I_{lim}$ the space charge region goes beyond the quasi-equilibrium electrical double layer at the interface. This causes a decrease in the effective thickness of the diffusion layer, thus providing the 'overlimiting' increase in the salt ion current. The study [398] has attracted considerable interest, since it gave a clue to the understanding of the mechanism of the 'overlimiting' current phenomenon. It was followed by a large number of studies concerning the role of the space charge in the formation of the 'overlimiting' current.[377, 378, 398–404, 448–452] Considerable progress was achieved due to a rigorous and, at the same time, rather simple solution of the Nernst–Planck–Poisson equations by Urtenov *et al.*[403, 448, 449] Assuming a quasi-uniform distribution of the space charge [403, 404] instead of the electroneutrality condition, in some instances the system of differential equations was reduced to a cubic algebraic equation.[403] This also permitted significant simplification of the method for solving the problem and studies of a three-layer system with two [451] and three types of ions.[452]

Simultaneously with the description of the structure of the diffusion layer at $I > I_{lim}$ many researchers [394, 399–402] attempted to simulate the mechanism of the appearance of convective fluid flows under the action of the electric field on the space charge (these flows destroy the diffusion layer). Currently, the electroosmotic slip mechanism, which was first proposed by Dukhin *et al.*[401] who called it electroosmosis of the second kind (since the space charge responsible for the onset of convection appears as a result of the current flow), is thought to be the most probable. Rubinstein *et al.*[377, 399, 400] reported a comprehensive analysis of electroconvection and showed that it appears in the near-surface region of both homogeneous and inhomogeneous membranes. The electroosmotic slip of a fluid can cause instability of concentration polarisation at the membrane, which manifests itself as oscillations of the electric potential jump, which transform into a random motion detected as an excess low-frequency electric noise at super-overlimiting currents. Urtenov *et al.*[394, 449] reported numerical calculations of electroosmotic vortices assuming a constant bulk electric force calculated using the Nernst–Planck–Poisson equations. The results obtained are in good qualitative agreement with those reported by Rubinstein.

Mention should be made that electroconvection is not the only form of a coupled convective motion of a fluid under intense current regimes. Gravitational convection also plays an important role in membrane systems, especially at rather high solution concentrations and large intermembrane distance.[396, 397] Under these conditions the Grashof [1] (or Rayleigh [377, 400]) numbers can exceed their critical values and convective flows develop in the system, destroying the diffusion layer. The contribution of electroconvection to the overlimiting current is more significant for dilute solutions at short intermembrane distances.[1, 394]

In conclusion it should be emphasised that concentration polarisation and transfer across the diffusion layer are of crucial importance for the formation of the properties of the whole membrane system. To follow how the properties of a membrane (in particular, its structure and kinetic parameters) affect the integral properties of the whole membrane system, one must know methods for description of the transfer processes occurring on different levels, namely, in a single membrane and in an assembly comprising a large number of membranes. In this case a hierarchic system of mathematical models [453] (some of them were briefly outlined above) may appear to be useful .

VI. Methods of investigations of ion transport in membranes

Conventionally, there are two avenues of research on the ion transfer in membranes. One of them involves comparison and optimum choice of membranes for various processes.[356, 454] Here, the main problem is the choice of the basic physicochemical (static and transport) characteristics of membranes, which would provide the greatest body of information, have unambiguous and clear physical meaning and be determined in not very time-consuming experiments without using sophisticated equipment.

On the other hand, measurements of physicochemical characteristics of membranes are required for basic research on the mechanism and quantitative description of ion transfer.

Numerous studies on the methods of chemical and thermodynamic research on ion exchange have been reported to date.[11,327] The diffusion layer characteristics are successfully determined by laser interferometry,[388,389] voltammetry,[409,420,455] chronopotentiometry,[372,409,456] using electrochemical noise[396,397,457] and impedance measurements,[416,417,456] *etc*. The electrochemical methods of investigations of the properties of ion-exchange membrane systems were reviewed by Pourcelly *et al*.[456]

In this Section we will dwell only on the methods for measuring the conducting and selectivity properties of membranes, due to which they occupy a special position among a variety of modern materials. These properties include first of all the conductivity, diffusion permeability and transport numbers of ions.[285–287,458,459] Below we briefly outline the electrochemical, ion exchange and spectroscopic methods used in this field of research.

1. Conductivity and transport numbers

Methods for measuring the ionic conductivity of solids are most often used for the description of the transport properties of various membrane materials, from inorganic salts and oxide systems to polymeric membranes. The area of their application extends from obtaining thorough knowledge of the nature of ionic mobility and its relation to the structure and surface to the practically valuable studies on fabrication of various electrochemical, membrane devices and power sources, in particular, fuel cells that have been the subject of intensive recent research.[4,460–462] In this connection it will be recalled that the well-known membrane polymeric material Nafion belongs to the proton solid electrolytes exhibiting the best conducting properties.[463,464]

The ionic conductivity is most often studied by impedance spectroscopy, which involves complex measurements of the ohmic and capacitive resistance of membranes. By plotting the impedance or admittance hodograph for a wide frequency range it is possible to determine the ionic conductivity of the material under study. Now we will outline the methods employed and point to some recent studies. Conduction studies of inorganic membranes,[465] various polyelectrolytes[159,461,462,466–469] and composite membranes[469,470] most often involve measurements of their impedance. Detailed description of the measuring techniques, measuring cells, as well as analysis of the results obtained using different types of equivalent circuits has been documented.[456–458,471–478] In particular, the use of impedance spectroscopy allows measurements of the diffusion coefficients of electrolyte in the diffusion layer and determination of the rate constants for water splitting in membrane systems.[414–417,439,479–482]

Since the conductivity of most membrane materials is strongly dependent on the water content,[351,458,461,462] considerable efforts have been made to control the water vapour pressure and maintain it at a constant level. However, even this approach precludes the choice of conditions identical to those realised in studies of the transport properties in aqueous electrolyte solutions. To ensure such conditions, experiments often involve conductivity measurements of membranes separating two electrolyte solutions containing the working electrodes.[456,458,477–478] The additional resistance of the solution is included by carrying out measurements for the same cell without the membrane (difference method). In some instances the solution resistance is comparable or higher than the membrane resistance. This causes a marked increase in the measurement error. Besides, interpretation of the results obtained is complicated by an additional contribution of the resistance of the membrane/electrode interfaces to the measured value and by possible deformation of the membranes in the cell.[458,478] Methods of solving this problem have been documented.[458,476–478]

A version of the difference method is the probe technique, which involves measurements using a four-electrode cell (two polarising and two working probe electrodes).[471] The use of two additional silver chloride or calomel electrodes permits simultaneous a.c. and d.c. measurements.[367]

The membrane d.c. frequency spectra measured under non-equilibrium conditions can also serve as a source of valuable information. To this end, a six-electrode cell can be used. One pair of electrodes is employed for the d.c. polarisation of the membrane under study, the other pair is used to induce an alternating sinusoidal electric field, while the third pair of electrodes acts as the potential probes. For simultaneous measurements of the membrane's voltage-*vs*.-current curve the cell is additionally equipped with two reversible reference electrodes. The use of such a measuring complex allows essential extension of the capabilities of membrane conductometry.[477]

A simple and rather accurate method for measuring the conductivity of ion-exchange materials representing both films and pieces of arbitrary geometry is the isoconductivity point technique.[354,355,458] It involves conductivity measurements of the solution with and without the ion exchanger in the conductometric cell.

Membrane selectivity depends on the mobility and concentration of ions in a given material. The basic characteristics of the ion-selective properties of a membrane are the transport numbers, which are defined as the electric charge transferred by a given type of ion in the absence of the pressure and concentration gradients. The fundamentals of the method for determination of the transport numbers of various solid and liquid objects were developed by Turbandt.[483]

The selectivity is often estimated by the e.m.f. method in a cell containing reversible electrodes and a membrane separating two solutions of different concentration.[484] In practice the so-called effective transport numbers, *i.e*., the fraction of the charge transferred in the presence of the concentration and pressure gradients, are most often determined.[485,486] To optimise the experimental design, it was proposed to use strong currents flowing over a short period of time;[484] closed cells with a concentration drop changing its sign in the course of the experiment;[444,487] devices for automatically maintaining the component concentrations at the cell inlet at a constant level,[394,488,489] *etc*.[444] To calculate the 'true' transport numbers, it was proposed to extrapolate the effective transport numbers to an infinitely strong current, since in this case the diffusion (not convection!) contribution to the flux can be neglected.[471]

A more detailed description of methods for measuring the transport numbers can be found in monographs.[307,308,444,472] It is appropriate to mention that liberation of some substances (*e.g*., oxygen) at electrodes in the case of volumetric control of the transfer process requires a rather high voltage. This can introduce errors into the results obtained as compared to those obtained under the conditions of impedance spectroscopy measurements.

Other electrochemical methods of investigations of transfer phenomena can also be rather informative. These include thermoelectric measurements, thermally stimulated depolarisation, Hall effect studies, *etc*.[472,474]

2. Spectroscopic methods

Various spectroscopic methods are often used in studies of transfer phenomena, ion and molecular mobility. One of them is vibrational spectroscopy.[165,490] However, NMR spectroscopy is the most important and promising. The advantages of this method are a broad range of characteristic frequencies and the possibility of description of the local environment of a given sort of atom. Since the energy of the dipole–dipole interactions is inversely proportional to the cubed distance between the dipoles, the shape and width of the line of a given nucleus are determined by its nearest environment only. This allows one to distinguish between the crystallographically nonequivalent positions in the crystal structure and to characterise the nearest environment of a given

type of nuclei.[491–494] In the case of a solid the rotation of the interatomic vector about the direction of the magnetic field at a frequency close to or higher than the resonance frequency causes averaging of the internuclear coupling. First of all, this manifests itself as line narrowing in the NMR spectra.[495] Analysis of changes in the widths or in the second moments of the NMR lines permits information on the rotational mobility in solids to be obtained.[180,494] Translational mobility of ions and molecules also leads to line narrowing, though the effect is much more pronounced in this case. The lines of the nonequivalent nuclei involved in the fast exchange merge together. Such studies allow determination of the characteristic frequency and the activation energy for this type of mobility.[494,496,497] The most valuable information on the cation mobility is provided by NMR relaxation in solids. Here, the researcher can immediately determine the frequency of rotational mobility and describe the processes of ion and molecular transfer. It should be noted that the activation energy for mobility extracted from the NMR data is often different from the data of electrochemical (in particular, impedance spectroscopy) measurements. The reason is that NMR spectroscopy gives the description of the local nuclear environment (see above), whereas the conductivity is undoubtedly an integral characteristic of a material. The predominant contribution to the overall process of transfer across the membrane may come from a low fraction of the atoms and ions possessing the highest mobility, *e.g.*, those located on the material's surface. Numerous examples of NMR studies of transfer processes have been documented.[87,166,494,496–502]

Another promising method for investigation of transfer phenomena in membranes is Raman spectroscopy,[456,503–506] which allows measurements of the vibrational spectra of the membrane components. This method provides particularly valuable information when the membrane contacts solutions of weak electrolytes. By Raman spectroscopy one can determine the concentrations of various ions (polychromates,[503] sulfates and hydrosulfates [504]), nitric acid and nitrates [505] in the membrane and in solution, as well as study poisoning of membranes in electrodialysis.[506]

3. Ion exchange rate and diffusion permeability measurements

The pioneering quantitative studies on the kinetics of ion exchange were carried out by Boyd, Adamson and Myers [324] who proposed a model, which treated an ionite grain as a homogeneous sphere. More recently, this model has been extensively used by Barrer and Falconer.[507,508] Up to now the results obtained in that time for the diffusion-controlled processes in a grain or film (adjacent diffusion layer) have been widely used in the same form to describe the kinetics of ion exchange. Processes involving diffusion in the ionite grain as the rate-determining stage predominate.

There are processes to which the above-mentioned model is inapplicable. Tunitskii *et al.*[509] and Helfferich [510–512] extended this model to the diffusion of ions possessing different mobilities and to the processes complicated by the occurrence of chemical reactions. According to another model proposed for ion exchange in a heterogeneous grain due to the movement of the interface between the initial and the newly formed phases, diffusion across a variable-thickness layer of exchange products occurs.[76,274,513]

A salient feature common to all these models is that the experimental data are obtained after disturbance of the equilibrated system by adding a reagent, which either contains a certain type of exchanging ion or, on the contrary, reduces their concentration due to complexation or formation of a weakly dissociating compound (*e.g.*, water). Then, the system relaxes to the equilibrium state. Here, the measured quantity is the continuously varied concentration of a particular sort of ions in the solution or in the ionite phase. In this connection such methods are called non-steady-state ones. The solution composition can be analysed by various analytical methods including potentiometric, polarographic and some other techniques.[161,273,274] It is commonly accepted that the drawback of this approach is the variable composition of the solution, which causes the driving force of the process to change and complicates its mathematical description.

To eliminate these problems, either the ratio of the solution volume to the ionite volume is increased or the so-called methods of infinitely large volume are used (a large volume of solution is rapidly passed through a thin ionite layer). The course of the process is assessed by analysing the changes in the composition of the sorbent phase.[55,514,515] This approach permits obtaining exact results but is very labour-consuming, which significantly limits the area of its application. In addition, the need for carrying out a continuous experiment can come into conflict with the necessity of frequent monitoring of the composition of the solid or liquid phase. More detailed studies of diffusion processes are also carried out using the methods based on the layer-by-layer analysis of cylindrical or conical ionite samples.[516–519]

Much less time-consuming are the isoconcentration methods involving compensation of the changes in the solution composition due to some external action. For instance, Haagen [519] who proposed this method studied the H^+/M^+ exchange reaction resulting in the formation of acid in solution. The acid formation changes the colour of an indicator. By adding the necessary amount of alkali the acid is neutralised and the colour is restored. The exchange rate can be estimated from the amount of alkali, which should be added during some time interval. More recently, this method was improved, namely, it was forced into the regime of automatic compensation of the liberating product and a number of novel methods for detection of disturbance of the system's equilibrium was implemented. Some other techniques were developed, which significantly extended the area of application of this method.[520,521]

Using planar membranes, one can investigate the transfer processes induced by various driving forces, namely, the concentration, pressure or electric potential gradients. The method of studying the diffusion processes induced by the concentration or the chemical potential difference of a particular sort of ion is the most similar to those considered above. A membrane is placed between two half-cells containing solutions with different concentrations of the permeate.[522–524] The method permits studies of the transfer processes proceeding at substantially different rates, as well as the processes occurring under quasi-steady-state or strongly nonequilibrium conditions.[524] This is first of all due to the possibility of varying the solution concentrations, cell volumes and the geometric parameters of the membrane (surface area, thickness). Besides, the chemical potential difference of a certain type of ion can be substantially increased by using reagents which react with these ions, thus resulting in the formation of complex, weakly dissociating or insoluble compounds.[524] A method for measuring the partial fluxes of particular types of ions through the membrane upon changes in the concentration and electric potential differences on each side of the membrane has been developed.[525] To improve the accuracy of the measurements, the pH value and the concentration of ions in the solutions circulating through both half-cells are automatically maintained at a constant level.

Studies of transfer through the membrane volume and elucidation of the role of the membrane surface require reliable data on the diffusion layer adjacent to the surface. Unfortunately, experiments with conventional flow cells are inappropriate for taking into account the role of the diffusion layer, since the layer thickness varies with coordinate and can be calculated only for plane-parallel geometry. Bobreshova *et al.*[526,527] developed the rotating membrane disk method, which significantly simplifies the solution to this problem, since it provides uniform accessibility of both sides of the membrane surface to mass transfer and permits calculations of the thickness of the diffusion layer. This method allows one to analyse the polarisation characteristics of the

membrane system and relatively easily distinguish between different stages of mass transfer.

Experimental methods for measuring the diffusion permeability of membranes can be conventionally divided into two groups: methods without and with solution flow. A non-flow cell for the first group of methods comprises two compartments separated by the membrane under study. One compartment is filled with an equilibrium solution with a prescribed electrolyte concentration, while the other compartment is filled with deionised water. The diffusion flow of electrolyte through the membrane can be assessed from, *e.g.*, an increase in the conductivity of the solution in the compartment filled with deionised water.[528] A drawback of such cells is that the electrolyte concentrations in both compartments vary with time. This limits the lower bound of the concentration to 0.01 mol litre^{-1}. The flow cell methods make possible extension of the concentration range and reduction of the lower bound of the concentration down to 10^{-4} mol litre^{-1}.[368]

The method for determination of the self-diffusion coefficients of the ions in membranes using radiotracers should be pointed out (for a review of related methods, see Ref. 129). As a rule, the self-diffusion parameters of the labelled ions can be measured with high accuracy.

Studies of the interdiffusion of ions in an external electric field and without it permit the determination of both the diffusion and electromigration mobility of the ions. If the dependence of these ion coefficients on the water content in the membrane is known, it is possible to draw some conclusions about the membrane microstructure. For instance, it was shown [529, 530] that an increase in the concentration of the solution in which the perfluorocarbon membrane is immersed (or a decrease in the membrane's water uptake) is accompanied by breakdown of large clusters into smaller ones and by shortening of the narrow cluster-connecting channels characterised by unidirectional diffusion of various ions. For cross-linked polystyrene sulfo cation-exchange membranes the above-mentioned coefficients are virtually independent of the solution concentration,[530] which is thought to be indicative of a rigid network microstructure of the membrane.

VII. Conclusion

Progress of membrane science is favoured by the wide use of membrane and ion-exchange materials in various industrial processes, water treatment, air cleaning, separation processes and the production of highly efficient power sources, *etc*. Various practically valuable applications require specific materials, which can operate in various media in different temperature regimes and possess high selectivity and chemical stability and specific mechanical properties. Because of this, a large number of novel membrane materials are synthesised and studied yearly, as well as new avenues and methods of application being proposed. In particular, the synthesis of novel composite membrane materials with prescribed properties has been the subject of considerable recent research. However, in all cases the ability of membranes to provide fast ion or molecular transfer is particularly important. From this standpoint the determining role is played by the methods for description of transfer phenomena.

The greatest body of information on the structure of and transfer processes in membranes can be obtained using complementary experimental methods of investigation. Notwithstanding common patterns of transfer phenomena in various inorganic and high-molecular-mass ion-exchange and membrane materials, it is impossible to correctly describe them without knowledge of the structural peculiarities and properties of these systems as well as phase transformations occurring in the course of exchange. In most cases of crucial importance is the use of different methods for theoretical description of these phenomena. At the same time interpretation of the experimental results and, hence, to a great extent their value are often limited to the existing mathematical models of the phenomenon under study. This particularly concerns the non-steady-state methods of investigation of transfer phenomena (chronopotentiometry, impedance), which have been rapidly developing recently. Description of these phenomena requires setting up of and solution of sophisticated mathematical problems. However, taking into account impetuous development of computational methods, rapid progress in this field also seems to be possible.

There is a great variety of transfer phenomena in membrane systems. However, the limited size of this review precluded consideration of many important problems in this area of study. Nevertheless, the authors hope that it will attract the attention of researchers to this field of investigation from both theoretical and practical standpoints.

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