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Molecular-kinetic Models of the Transfer of Substances in Inorganic Membranes

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Molecular-kinetic models of the transfer of susbstances through crystalline inorganic membranes have been examined, taking account of the influence of the principal real properties of the system: the interaction between the particles adsorbed on the surface and between the particles dissolved in the volume of the membrane; the non-uniformity of the region of the solid next to the surface; the restricted mobility of the particles; and the change in the state of the volume phase during the transfer of the diffusing substance. The possibility of applying these models to the problems of transfer through vitreous inorganic and polymeric membranes has been discussed.
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I. INTRODUCTION

Inorganic membranes represent a wide range of inorganic compounds which can be used to separate mixtures of substances. The materials used for inorganic membranes include metals, alloys, metal oxides, silicate glasses, ionic crystals, and zeolites.

The problem of the transfer of hydrogen in metals and alloys is of the greatest scientific and technical importance. It is related to the solution of a large number of problems: the purification and enrichment of gas mixtures;[1-3] membrane catalysis, used in hydrogenation and dehydrogenation processes to obtain highly pure substances, monomers for synthetic materials, intermediates for the production of vitamins, drugs, and dyes;[4,5] hydrogen power engineering,[3,6] etc. The higher permeability of silver catalysts[4,5] and catalysts based on simple and complex oxides[7-10] towards oxygen is also used in membrane catalysis to increase the selectivity of redox processes. Silicate glasses and ionic crystals are widely used to obtain membranes for ion-selective electrodes, used in analysis.[11] The high permeability of glasses towards inert gases, particularly helium,[1,2] is a prerequisite for the technical application of the glasses in gas-separation processes. Molecular sieves based on natural and synthetic zeolites[12,13] have widely different permeabilities for different substances, so that they can be used in gas separation and membrane catalysis.

Inorganic membranes have a high selectivity and increased mechanical strength and thermal stability compared with membranes based on organic polymers, and this makes them irreplaceable at high temperatures.

A basis for the description of the processes of mass transfer through membranes[14-40] is provided by the following scheme (Fig.1). The stream of the substance is supplied to the membrane surface *a*, where it is adsorbed and dissolves in the region next to the surface. The substance diffusing then passes through the volume phase of the membrane and leaves it through the surface *b*. In Fig.1, *k* denotes the number of the crystallographic layers perpendicular to the direction of the flow of the substance; the thickness of these layers is approximately equal to the diameter of the particles of the substance diffusing. κ_a and κ_b denote the thickness of the membrane surface regions, whose properties may differ considerably from one another and from those of the bulk phase. In the general case, $\kappa_a \neq \kappa_b$; in most of the works cited, it is assumed that $\kappa_a = \kappa_b = 1$.

Models of the processes involved in the solution and transfer of substances in solids are based on diffusion equations, supplemented by appropriate boundary conditions. Various questions related to the derivation of expressions for the diffusion coefficient and the search for boundary conditions based on a discrete scheme of randomly moving particles,[22,36] the role of saturation of the volume and the surface by the particles of the substance diffusing,[14-17,19,21,23,24,26,29] allowance for the non-equilibrium character of the processes in the surface regions and in the bulk of the membrane,[18,20,25,27,28,30,32,34,35,37,38,40] and the influence of the asymmetry of the membrane and the contribution of surface and volume defects[31,33,35,39] have been examined in detail.

In the one-dimensional model, the values of the local concentrations of the particles are related to a particular layer *k*; these values are the average values in the volume of the given layer. In macro-non-uniform systems, this scheme may be over-simplified. In layer and composite membranes, it is necessary to take more detailed account of the distribution of the non-uniform regions of the membrane within each layer,[41,42] and this makes it necessary to use two-dimensional instead of one-dimensional models of the transfer process.

All the models used at present are based on the description of the rates of the elementary processes of adsorption–desorption and migration of the particles from the law of mass action,[43] which assumes that all the particles are distributed randomly and that each behaves independently of the others. This assumption is justified only when the concentration of the particles is low. Another important assumption made in most models of mass transfer is the assumption (explicit or implicit) that the membrane is inert and that its role reduces to the determination of the sequence and inter-relationship of the absorption centres (these are usually interstices) involved in the transfer of the particles.

In many situations, these assumptions do not reflect the real properties of the systems and the conditions under which the transfer processes take place, since they are made without allowance for complex cooperative effects. Two groups of cooperative effects can be distinguished. The first is associated with a high density of sorbed particles. Most of the sorbed particles form a relatively strong bond with the solid, leading to their adsorption on the surface and absorption in the volume. The total quantity of sorbed molecules may be comparable with the number of adsorption and absorption centres. In this situation, the average distance between the sorbed particles is comparable with their dimensions, and at these inter-particle distances, appreciable interactions are possible (the nature of these interactions will not be made more specific here[44–47]). This leads to the appearance of different phase states of the sorbed particles, in particular their separation into layers and (or) ordering.[47–50] The phase state of the sorbed particles depends on their local concentration and on the temperature of the system.

The second group of cooperative phenomena is associated with the interaction of the sorbed particle with the atoms of the solid, leading to a change in the distribution of the components of the membrane in the bulk and in the surface regions, compared with their distribution in the absence of the molecules of the gas phase. In many cases, hydrogen and oxygen form chemical compounds with metal atoms, leading to a change in the properties of the membranes (a whole series of solid solutions with variable composition may be formed). This is reflected in the appearance of hysteresis on the sorption–desorption graph, an increase in the volume of the metal when the stream of gas passes through it, cracking of the metal, etc.[51,52] The energy stresses arising when hydrogen is dissolved have been estimated.[53] Similar cation redistribution phenomena are observed in solid electrolytes[54,55] and zeolites.[12] The nature of the change in the state of the solid depends on the intensity of the flux of the diffusing substance.

II. THE INFLUENCE OF INTERACTIONS BETWEEN THE PARTICLES ON THE RATES OF THE ELEMENTARY PROCESSES

The cooperative character of the transfer processes influences primarily the rates of the elementary processes. The transfer of a substance through a membrane consists of at least two stages: adsorption–desorption and migration. If the membrane is a catalyst, stages involving the adsorption and desorption of another reagent and the stage of chemical transformation also take place on one of its sides. The interactions between the particles influence the rates of each stage, and hence the rate of the overall process.

The description of the rates of the elementary processes will be based on the fundamental postulates of the theory of absolute reaction rates,[56] the initial version of which is applicable to ideal systems, that is to systems of non-interacting particles.

It is not possible to take formal account of the non-ideal nature of the system[56–58] using the activity coefficients of the reagents and the activated complexes, since the calculation of the activities in turn requires model representations of the interactions between the particles and of the structure of the condensed phase. When allowance is made for the interaction of neighbouring particles,[59] the generalisation of the expression derived from the theory of absolute reaction rates leads to a change in the concentration dependence of the rates of the elementary processes. The reason for this can be illustrated for the bimolecular reaction $iZ + jZ$, where i, j = A or v, AZ is an adsorption centre occupied by a particle A, and vZ is an unoccupied centre. With this notation, the stage involving the adsorption of an A_2 molecule is written as $A_2 + 2vZ \rightleftarrows 2AZ$, and the stage involving the migration of the particles is written as $AZ_k + vZ_q \rightleftarrows vZ_k + AZ_q$, where the indices k and q correspond to the numbering of neighbouring centres in the volume or on the surface. A uniform lattice in which each site has z neighbours can be

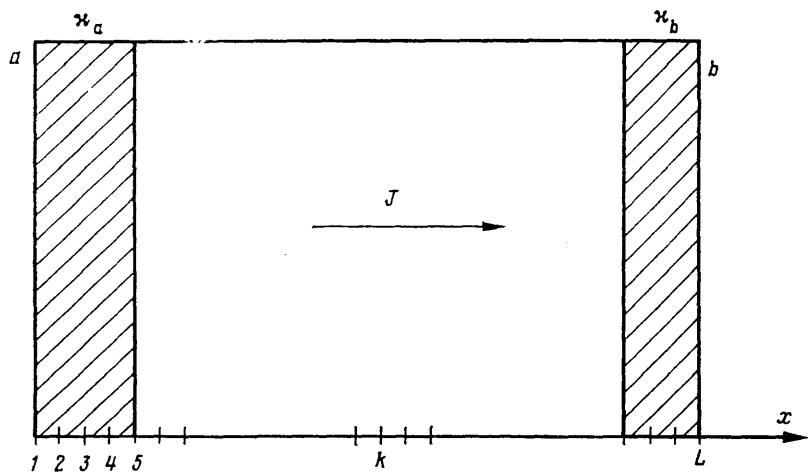


Figure 1. Diagram of a membrane; k is the layer number, κ_l is the thickness of the surface region l, $l = a, b$.

considered. For planar lattices, the sites correspond to adsorption centres, and for these, $z = 3$, 4, or 6; in volume lattices, the sites correspond to absorption centres, and for these, $z = 4$, 6, 8, or 12.

When there is no interaction between the particles, the rate of the reaction $iZ + jZ$ is expressed as $V_{ij} = k_{ij}\theta_i\theta_j$, where k_{ij} is the reaction rate constant, and $\theta_i(\theta_j)$ the concentration of the component $i(j)$ (its mole fraction), which characterises the probability that any site of the lattice is occupied by a particle of type $i(j)$. (Subsequently, quantities relating to different regions of the lattice: on the surface, in the bulk, or in a specific layer of the membrane, will be distinguished.) The normalisation condition is

$$\sum_{i=1}^{s} \theta_i = 1,$$

where s is the number of components of the system, including the unoccupied sites v. Usually,

$$k_{ij} = \hat{k}_{ij}\exp(-\beta E_{ij}),$$

where E_{ij} is the activation energy of the reaction, $\beta = (kT)^{-1}$, and k_{ij} the pre-exponential factor in the expression for the rate constant. If $i = j = A$, then k_{AA} is the rate constant of the desorption; if $i = A, j = v$ (or vice versa), then k_{Av} is the rate constant of the migration; if $i = j = v$, then $k_{vv} = k_{vv}p_{A_2}\exp(-\beta E_{vv})$ is the effective rate constant of the adsorption, where the partial pressure of the molecules of the gas phase p_{A_2} has been included to ensure uniform-ity of the form of the expression for the rate V_{ij}.

The influence of the interaction of neighbouring particles is revealed primarily by the fact that the height of the activation barrier of the elementary reaction changes with change in the local composition. $E_{ij}(n\sigma)$ denotes the energy of the interaction of the reagents ij with their neighbours in the ground state, and $E^*_{ij}(n\sigma)$ the energy of the interaction of the activated complex with its neighbours in the transition state. The configuration of neighbouring particles is given by the indices n and $\sigma(n)$, where n defines the number of neighbouring particles A in the sites of the first coordination sphere around the pair of reagents ij, and $\sigma(n)$ defines the way in which they are arranged for a fixed value of n (Fig.2). The difference $E^*_{ij}(n\sigma) - E_{ij}(n\sigma)$ gives the change in the height of the activation barrier for a given local configuration $n\sigma$. For a fixed position of all neighbouring particles, the rate of the elementary process at the two central sites is written as follows:

$$V_{ij}(n\sigma) = k_{ij}\theta_{ij}(n\sigma)F_{ij}(n\sigma),\quad F_{ij}(n\sigma) = \exp\beta[E^*_{ij}(n\sigma) - E_{ij}(n\sigma)]. \qquad (1)$$

where $\theta_{ij}(n\sigma)$ is the probability of existence of the configuration $n\sigma$ round the central particles ij. This quantity is the probability of a complex event, and to determine the reaction rate it must be expressed in terms of θ_i.

The expression for the rate V_{ij} of the reaction being considered, related to the entire surface, is obtained by averaging the expression (1). If $\alpha_{ij}(n\sigma)$ denotes the statistical weight of the configuration $n\sigma$, then

$$V_{ij} = k_{ij}\sum_{n}\sum_{\sigma(n)}\alpha_{ij}(n\sigma)\theta_{ij}(n\sigma)F_{ij}(n\sigma) \qquad (2)$$

where the first summation is carried out over the number of particles n, and the second is carried out over the different configurations $\sigma(n)$ for a fixed value of n. The set of configurations of particles A for a planar lattice with $z = 4$ is shown in Fig.2.

The paired interactions between nearest neighbours can be taken into account.[59] ε_{ij} denotes the magnitude of the interaction of particles i and j occupying neighbouring sites and present in the free state. Naturally, $\varepsilon_{ij} = \varepsilon_{ji}$. If one of the particles is an unoccupied

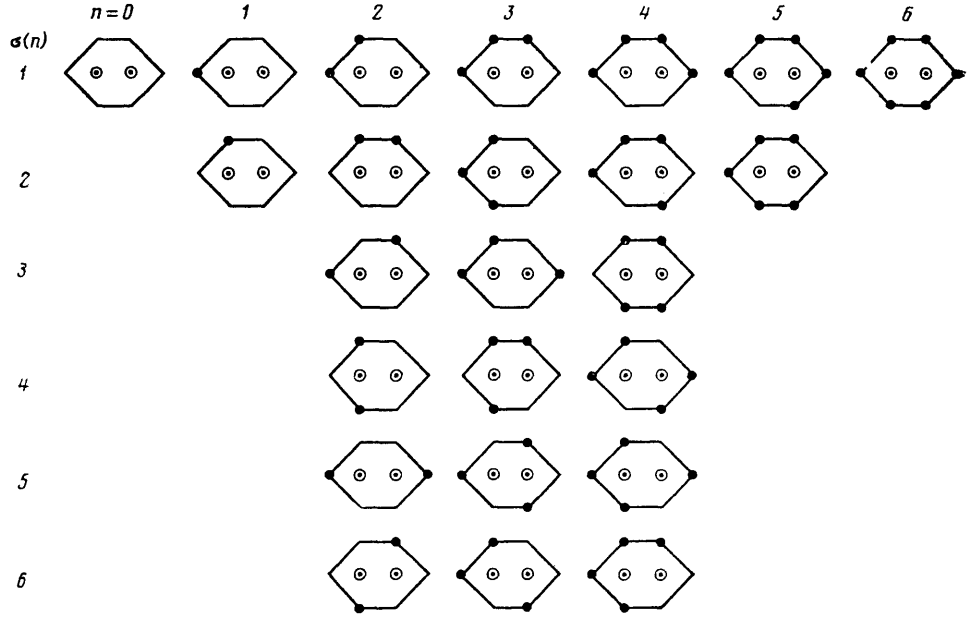


Figure 2. Configurations of particles A in the first coordination sphere round the central particles in a square lattice; the light circles represent the central particles, and the black circles the adsorbed particles A.

site, then $\varepsilon_{iv} = 0$. The formation of the activated complex involves the transfer of particles from the ground state to the activated state, corresponding to a change in the positions of the reagents relative to their neighbours. The energy of the interaction of the reagent i with a neighbouring particle j in this transition state is denoted as ε^*_{ij}. Although $\varepsilon^*_{iv} = 0$, nevertheless $\varepsilon^*_{vA} = \varepsilon^*_{AA}$, since the interaction of the activated complex with its neighbours is independent of the direction of the reaction. For paired interaction of the particles, the magnitude of $E_{ij}(n\sigma)$ is independent of the way in which the particles are arranged:

$$E_{ij}(n\sigma) = \varepsilon_{ij} + \varepsilon_{iA}n_1 + \varepsilon_{iv}(z-1-n_1) + \varepsilon_{jA}n_2 + \varepsilon_{jv}(z-1-n_2) \quad (3)$$

where n_1 and n_2 are the numbers of particles A around the particles $i(n_1)$ and $j(n_2)$, so that $n_1 + n_2 = n$. This expression has the following structure: the term ε_{ij} corresponds to the interaction of the original reagents, the next two terms correspond to the interaction of the particle i with its neighbours, and the last two terms to the interaction of the particle j with its neighbours. One of the sites closest to each central site is occupied by the other reagent, and the remaining $z - 1$ sites are occupied by neighbouring particles. For the activated complex, the interaction of its fragments "i and j" relates to the internal energy, so that in the expression for $E^*_{ij}(n\sigma)$, the first term ε_{ij} is not present, and the other terms contain ε^*_{ij} instead of ε_{ij}. This leads to the expression

$$F_{ij}(n\sigma) = \exp\beta[-\varepsilon_{ij} + n_1\delta\varepsilon_{iA} + (z-1-n_1)\delta\varepsilon_{iv} + n_2\delta\varepsilon_{jA} + (z-1-n_2)\delta\varepsilon_{jv}] \quad (4)$$

where $\delta\varepsilon_{ij} = \varepsilon^*_{ij} - \varepsilon_{ij}$.

Only one of the simplest methods of calculating the functions $\theta_{ij}(n\sigma)$ will be considered. It will be assumed that all the configurations with different $\sigma(n)$ are equally probable [for example, $\theta_{ij}(31) = \theta_{ij}(34)$]. Taking account of the distribution of the particles A in neighbouring sites round different central particles, it is then possible to write:

$$\sum_{\sigma(n)} \alpha_{ij}(n\sigma) = C^{n_1}_{z-1}C^{n_2}_{z-1},$$

where $C^{n_1}_{z-1}$ is the number of combinations of n_1 from $z - 1$. The function $\theta_{ij}(n\sigma)$ can be written as

$$\theta_{ij}(n\sigma) = \theta_{ij}t_{iA}^{n_1}t_{jA}^{n_2}t_{jv}^{z-1-n_1}t_{jv}^{z-1-n_2}$$

This form of expression indicates that the probability of a given many-particle configuration is approximated by the probabilities of simpler events, namely the probability of finding the particle i (θ_i) and the probability of finding the particles i and j in a pair of neighbouring sites (θ_{ij}): $t_{ij} = \theta_{ij}/\theta_i$, where t_{ij} is the conditional probability of finding a particle j next to a particle i; $\theta_{iA} + \theta_{iv} = \theta_i$. This is the so-called quasi-chemical approximation.[60,61] With allowance for the foregoing, including Eqn.(4), the expression (2) can be rewritten as follows:[59,64,67]

$$V_{ij} = k_{ij}\exp(-\beta\varepsilon_{ij})\sum_{n_1=0}^{z-1} C^{n_1}_{z-1}\Phi_{iA}^{n_1}\Phi_{iv}^{z-1-n_1} \times \times \sum_{n_2=0}^{z-1} C^{n_2}_{z-1}\Phi_{jA}^{n_2}\Phi_{jv}^{z-1-n_2} = k_{ij}\exp(-\beta\varepsilon_{ij})(S_iS_j)^{z-1} \quad (5)$$

where

$$S_i = \Phi_{iA} + \Phi_{iv}, \quad \Phi_{ij} = t_{ij}\exp(\beta\delta\varepsilon_{ij})$$

In the general case of an arbitrary number of components s, the functions θ_{ij} can be determined in terms of the concentrations of the particles by solving the system of equations (equilibrium distribution of the particles):[61]

$$\theta_{ii}\theta_{jj} = \theta_{ij}^2\exp[\beta(\varepsilon_{ii} + \varepsilon_{jj} - 2\varepsilon_{ij})], \quad \sum_{i=1}^{s}\theta_{ij} = \theta_i, \quad \sum_{i=1}^{s}\theta_i = 1 \quad (6)$$

The expressions for the rates of the elementary processes taking place on one and on two sites can be written in the form:[59]

$$V_i = k_i\theta_i(S_i)^z, \quad V_{ij} = k_{ij}\exp(-\beta\varepsilon_{ij})\theta_{ij}(S_iS_j)^{z-1}, \quad S_i = \sum_{j=1}^{s} t_{ij}\exp(\beta\delta\varepsilon_{ij}) \quad (7)$$

When the particles interact, the form of the expressions for the reaction rates changes as a result of the appearance of the functions S_i and as a result of the change in the probability that the reagents meet ($\theta_{ij} \neq \theta_i\theta_j$). When the reaction rates of each stage in the forward and back directions are equal, the equilibrium relationships between the concentrations of the particles are obtained with allowance for the interaction between nearest neighbours.[59] The interactions between the particles alter considerably the kinetic characteristics of the adsorption–desorption processes[62–64] They justify the empirical equations of Becker and Langmuir for the rate of desorption and of Zel'dovich and Roginskii for the rate of adsorption in chemisorption on uniform surfaces (the linear dependence of the logarithms of the rates of the processes on the degree of coverage) and the power dependence of the rate of desorption on the degree of coverage (Benham–Bart–Kwan kinetics),[65] and explain the existence of ranges corresponding to rapid and slow chemisorption.[66] The effects of correlation between particles being repelled leads to the splitting of the thermodesorption spectra on a uniform surface.[63]

Eqns.(7) can be used to estimate the self-diffusion coefficient D^*_i, characterising the transfer of a labelled component i under equilibrium conditions.[59,67,68] θ^*_{ik} denotes the fraction of the labelled component i in the layer k. The flux of the labelled particles J in the direction of the x axis is represented as the difference between the numbers of labelled particles A transferred in unit time into neighbouring vacancies from the layer k into the layer $k + 1$ and vice versa:

$$J = k_{iv}(\theta^*_{ik} - \theta^*_{i,k+1})t_{iv}(S_iS_v)^{z-1} \quad (8)$$

Comparison of this equation with the expression for Fick's first law ($J = -D^*_i d\theta^*_i/dx$) with the condition that the change in the concentration of labelled particles between neighbouring layers is small ($\theta^*_{i,k+1} = \theta^*_{ik} + ad\theta_i/dx$, where a is the lattice parameter) gives:

$$D^*_i = a^2k_{iv}t_{iv}(S_iS_v)^{z-1} \quad (9)$$

Expressions for the self-diffusion coefficient taking account of the interaction between the particles using other approximations, and for other mechanisms of migration, are obtained analogously.[69] In multi-component systems, the concept of self-diffusion coefficient is defined in different ways.[69] Nevertheless, in each specific case, it can be expressed in terms of the rates of jumping of the particles. In general, the situation is more complex than described here in terms of the traditional approach.[56,69] The complication is due to the fact that, for a number of mechanisms, there is a correlation between successive jumps of the particles, leading to the appearance of a correlation factor in Eqn.(9).[69] According to available estimates, for a binary system in the absence of interaction it varies from 1 to 0.65 for $0 \leqslant \theta \leqslant 1$.[70] This model has been used[71] to explain the anomalously low values of the activation energies of self-diffusion in the metals γ-U, β-Ti, and β-Zr.[72]

The expressions obtained for the elementary processes make it possible to construct kinetic equations describing the change in the surface concentrations of adsorbed species during surface reactions. These reactions, on the one hand, are of fundamental interest for membrane catalysis, and on the other hand define the boundary conditions for the processes of mass transfer through a membrane. The form of these equations can be examined for a model example. It will be assumed that the following three-stage process takes place: 1) $A_2 + 2Z \leftrightarrows 2AZ$, 2) $B + Z \leftrightarrows BZ$, 3) $AZ + BZ \rightarrow 2Z + C$. The first stage may represent, for example, the dissociative adsorption of hydrogen molecules in hydrogenation or dehydrogenation, or the adsorption of oxygen molecules in redox reactions. The second stage corresponds to the adsorption of the other reagent, and the third to the formation of the product C. If the given process takes place on one side of a membrane with a uniform surface, the kinetic equations have the form (in the adsorption system, three components are considered: A, B, and v):

$$\begin{gathered}\dot{\theta}_A = z[V_{vv}(1) - V_{AA}(1) - V_{AB}(3)] \\ \dot{\theta}_B = V_v(2) - V_B(2) - zV_{AB}(3) \\ \theta_A + \theta_B + \theta_v = 1\end{gathered} \tag{10}$$

The significance of the terms on the right-hand sides of Eqns.(10) can be seen from Eqns.(7); they contain the additional indices of the stage numbers ($\alpha = 1, 2, 3$), since the parameters of the interaction $\varepsilon_{ij}^{*}(\alpha)$ are different for different stages. If the reaction involves the molecules of the gas phase, the effective reaction rate constant contains as a factor the partial pressure of the substance involved in the given stage α.

If the process takes place on a catalytic membrane and the component A is transferred through it to the surface b on which the component B is adsorbed, the kinetic equations for the component A on the different surfaces have the form:

surface a:

$$\dot{\theta}_A = z[V_{vv}(1) - V_{AA}(1)] - I_A(a)$$

surface b:

$$\dot{\theta}_A = I_A(b) - zV_{AB}(3) \tag{11}$$

where the term $I_A(l)$, $l = a, b$ denotes the flux of the particles A from the surface l into the bulk of the membrane (the expression for I_A is given in the next section). The process of transfer of the component A corresponds to the stage $\alpha = 4$. The kinetic equation for the component B relates to the surface b, and its form coincides with that of expression (10).

The kinetic equations (10) and (11) are based on Eqns.(6) and (7), which are applicable when the surface mobility of the particles is high, ensuring their equilibrium distribution. This situation is apparently always realised for hydrogen atoms. For the atoms of oxygen and other moleecules, denoted B, it is possible to have situations in which the rate of their migration is comparable with the rate of the elementary reactions. The system of kinetic equations (10) and (11) must then be altered,[73,74] since Eqns.(6) are replaced by the kinetic equations for the functions θ_{ij}.

III. EQUATIONS FOR THE TRANSFER PROCESS

It is simplest to examine the characteristic features of models with restricted mobility of the particles for the case of the migration process. It will be assumed that the component A is transferred in the volume of the membrane through the interstices (vacancy mechanism). The concentration of particles in the layer k, denoted by θ_k, changes as a result of the exchange of the particles with the vacancies of neighbouring layers:[75]

$$\dot{\theta}_k = -z_{k,k-1}(V_{k,k-1}^{Av} - V_{k,k-1}^{vA}) - z_{k,k+1}(V_{k,k+1}^{Av} - V_{k,k+1}^{vA}) \tag{12}$$

where z_{kq} is the number of sites in the layer q, adjacent to a site in the layer k;

$$q = k,\ k \pm 1,\ \sum_q z_{kq} = z_k,$$

and z_k is the number of neighbouring sites for a site in the layer k. For uniform lattices, the numbers z_k and z_{kq} are constant for all the layers, whereas for non-uniform lattices these numbers are different. The quantity V_{kq}^{Av} is the rate of migration of a particle A from a site of the layer k into a vacancy of the layer q.

$$V_{kq}^{Av} = k_{Av}\theta_{kq}^{Av} \prod_{p=k+1}^{k-1} [S_{kp}^{A}(4)]^{z_{kp}-\Delta_{qp}} \prod_{p=q+1}^{q-1} [S_{qp}^{v}(4)]^{z_{qp}-\Delta_{kp}} \tag{13}$$

where Δ_{kq} is the Kronecker symbol, and the functions S_{kq}^{i} represent the generalisations of Eqns.(7) for the case of a non-uniform distribution of the particles in the lattice sites:

$$S_{kq}^{i}(\alpha) = \sum_{l=1}^{s} \theta_{kq}^{il} \exp[\beta\delta\varepsilon_{il}(\alpha)]/\theta_k^i \tag{14}$$

Eqns.(13) and (14), obtained in the quasi-chemical approximation, show that the right-hand sides of Eqns.(12) contain the unknown functions θ_{kq}^{ij}, that is the system of equations (12)–(14) is not closed. In Eqns.(12) the same migration process leads to a change in the concentration of the particles in each layer and a change in the concentration of pairs of neighbouring particles, influencing through the inter-particle interaction the height of the activation barrier of the elementary process. Thus for the system of kinetic equations (12) to be closed, it is necessary to add to it the kinetic equations for the functions θ_{kq}^{ij}. With allowance for the normalisation relationships

$$\sum_{j=1}^{s} \theta_{kq}^{il} = \theta_k^i; \quad \sum_{i=1}^{s} \theta_{kq}^{il} = \theta_q^l; \quad \sum_{i=1}^{s} \theta_i = 1 \tag{15}$$

For the binary system A–v, it is sufficient to introduce one equation for the function θ_{kq}^{AA}:

$$\dot{\theta}_{kq}^{AA} = -\sum_{h=k+1}^{k-1} (z_{kh} - \Delta_{qh})[V_{hkq}^{\overline{vA}A} - V_{hkq}^{\overline{Av}A}] - \sum_{h=q+1}^{q-1} (z_{qh} - \Delta_{kh})[V_{kqh}^{A\overline{Av}} - V_{kqh}^{A\overline{vA}}]$$

$$V_{hkq}^{\overline{vi}l} = V_{hk}^{vi}\psi_{kq}^{il}, \quad \psi_{kq}^{il} = \theta_{kq}^{il}\exp[\beta\delta\varepsilon_{il}]/(\theta_k^i S_{kq}^l) \tag{16}$$

where the first summation corresponds to the migration of a particle A from the layer k into a neighbouring site of the layer h and back again, and the second summation corresponds to the migration of another particle A from the layer q into a neighbouring site of the layer h. The terms of Eqns.(16) are expressed in terms of the rates of the elementary processes (13); the "reacting" species are indicated by a bar above the symbol. The functions ψ_{kq}^{ij} take account of the influence on the rate of change in θ_{kq}^{AA} of a neighbouring particle not taking part in the elementary process at the given moment of time.

The equations for the functions θ_{kq}^{ij} are constructed assuming that after a characteristic short time interval, only one elementary process takes place.[73–76] Finally, the system of equations (12)–(16) is closed and is solved with the specified initial conditions $\theta_k(\tau = 0)$ and $\theta_{kq}^{AA}(\tau = 0)$, $q = k, k + 1$. Equations for the θ_{11}^{ij} for restricted mobility of the reagents on the membrane surface, supplementing Eqns.(10) or (11) for the model process being considered, are given in Ref.76.

Thus restricted mobility of the particles must lead to the appearance of equations for the paired distribution functions θ_{kq}^{ij} (or for t_{kq}^{ij}). This applies to diffusion-controlled reactions,[36] ideal models of systems with a high concentration of particles[70,77] and single-layer transfer,[78] and ideal models of transfer processes with an arbitrary concentration of particles.[73-76,79]

The phase interface produces a change in the properties of the surface regions of solids. This is revealed in a change in the distance between the surface crystallographic layers and the lattice parameter in the layers, and also in structural transitions and a change in the concentration profile of the surface region.[80-83] As a result, there is a change in the properties of the absorption centres in the surface region. Study of the surface properties shows that outside the critical range, the thickness of the surface region does not exceed 5–10 layers,[82-85] but its non-uniformity may have a considerable influence on the characteristics of the membrane permeability. In the surface region, the structure of Eqns.(12)–(16) remains unchanged (the layer $k = 1$ corresponds to the surface layer of adsorbed particles), but in the terms it is necessary to replace the parameters ε_{ij}, ε_{ij}^{*}, and k_{Av} by the analogous parameters ε_{kq}^{ij}, ε_{kq}^{ij*}, and k_{kq}^{Av}, depending on the layer number. Thus $I_{\mathrm{A}}(a) = V_{12}^{\mathrm{Av}} - V_{12}^{\mathrm{vA}}$, and analogous expressions are applicable for $I_{\mathrm{A}}(b)$.

For long times ($k_{\mathrm{Av}}\tau \gg 1$), instead of the discrete system of equations, it is possible to use the diffusion equation

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial}{\partial x}\left(D(\theta)\,\frac{\partial\theta}{\partial x}\right);\quad x = (k-\varkappa)\,a \tag{17}$$

for which the system of equations for $0 \leqslant k \leqslant \kappa$ represents the boundary condition relating the bulk value of the concentration θ to the concentration of particles in the gas phase. In the diffusion approximation, $\dot{\theta}_{\kappa-1}^{\mathrm{A}} = 0$,[29,75] so that the equation for the layer $\kappa - 1$ can be written in the form

$$D(\theta)\,\frac{d\theta}{dx} + z_{\varkappa-1,\varkappa-2}\,(V_{\varkappa-1,\varkappa-2}^{\mathrm{vA}} - V_{\varkappa-1,\varkappa-2}^{\mathrm{Av}}) = 0 \tag{18}$$

The form of the other equations in the surface region depends on the relationship between k_{Av} and k_{kq}^{Av}. If $k_{kq}^{\mathrm{Av}}\tau \ll 1$, it is necessary to use the original system of differential equations; otherwise, for all intermediate layers $\dot{\theta}_k^{\mathrm{A}} = 0$, leading to the appearance of an algebraic relationship between $\theta_{\mathrm{A}}(x = 0)$ and the pressure of the molecules in the gas phase. For $k_{kq}^{\mathrm{Av}} \leqslant k_{\mathrm{Av}}$, this relationship is determined by the steady-state relationships $\dot{\theta}_k^{\mathrm{A}} = 0$, and for $k_{kq}^{\mathrm{Av}} \gg k_{\mathrm{Av}}$ it is determined by equilibrium relationships of type (6).[86] The change to the diffusion approximation also corresponds to the steady-state condition for the kinetic equations for the functions θ_{Av} in the volume of the solid. For a qualitative estimate of the diffusion coefficient (mass transfer) it is possible to use the condition of local equilibrium distribution of the particles.[71] In Ref.71 it was found that in the range of separation into layers, the diffusion coefficient may take negative values (condensation of the substance diffusing). A mathematical description was also obtained for experimental data[87] on the diffusion of oxygen atoms on the (110) face of tungsten. In the surface layers, the equations for $\theta_{kq}^{\mathrm{Av}}$ either remain differential, if $k_{kq}^{\mathrm{Av}}\tau \ll 1$, or become steady-state algebraic relationships of the form $\dot{\theta}_{kq}^{\mathrm{Av}} = 0$, if $k_{kq}^{\mathrm{Av}} \lesssim k_{\mathrm{Av}}$, or into equilibrium algebraic relationships,[86] if $k_{kq}^{\mathrm{Av}} \gg k_{\mathrm{Av}}$.

IV. EQUATIONS FOR THE CHANGE IN THE STATE OF THE MEMBRANE

If the interaction between the atoms of the solid and the particles being transferred is sufficiently strong, it may lead to a change in the state of the membrane in the bulk. The non-equilibrium distribution of the substance diffusing along the thickness of the membrane leads to a redistribution of the atoms of the solid both along the thickness of the membrane and within each layer. If it is assumed that the particles of the substance diffusing migrate through the interstices of an alloy, and that the atoms of the alloy migrate, in accordance with the vacancy mechanism, through substitution lattice sites, then there arises the problem of describing the processes involved in the migration of particles of different kinds in different sub-lattices (immiscibility of the particles of different sub-lattices). For clarity, the treatment will be restricted to the case of a disordered alloy with a face-centred cubic (FCC) lattice, in which the dissolved particles occupy only octahedral interstices. The distances between the atoms of the alloy and between the particles of the substance diffusing in neighbouring interstices are greater than the distance between a particle and a neighbouring atom; in the general case, therefore, it is necessary to examine the problem in which account is taken of the interactions of not only nearest neighbours, but also more distant neighbours.[88-90]

The symbol γ will be used to denote the sites of the substitution sub-lattice of the alloy, and the symbol δ to denote the sites of the interstice sub-lattice. The equations for the evolution of the components of the alloy in the direction of the flux of diffusing substance will then have the form:

$$\dot{\theta}_k^{i}(\gamma) = -z_{k,k-1}\,[V_{k,k-1}^{i\mathrm{v}}(\gamma\gamma) - V_{k,k-1}^{\mathrm{v}i}(\gamma\gamma)] - z_{k,k+1}\,[V_{k,k+1}^{i\mathrm{v}}(\gamma\gamma) - V_{k,k+1}^{\mathrm{v}i}(\gamma\gamma)] \tag{19}$$

where $\theta_k^{i}(\gamma)$ is the mole fraction of the atoms i in the sites of the sub-lattice γ of the layer k. The structure of Eqns.(19) coincides with that of the equation for the transfer of the substance diffusing (12), which also remains applicable in the present case if its left-hand side contains $\theta_k^{\mathrm{A}}(\delta)$, and its right-hand side the terms $V_{kq}^{\mathrm{Av}}(\delta\delta)$. The indices in brackets indicate the sites of the sub-lattices containing the migrating atoms and particles, and also the vacancies. The terms of Eqns.(19), according to Ref.90, have the form ($\lambda = \gamma, \delta$):

$$V_{kq}^{i\mathrm{v}}(\gamma\lambda) = \hat{k}_{i\mathrm{v}}\theta_{kq}^{i\mathrm{v}}(\lambda\lambda)\prod_{h=k+k_R}^{k-k_R}\prod_{r_h}\prod_{\sigma}[S_{kh}^{i}(\lambda\sigma\,|\,r)]^{\varkappa_{qh}(\lambda\sigma|r)} \times \prod_{h=q+k_R}^{q-k_R}\prod_{r_h}\prod_{\sigma}[S_{qh}^{\mathrm{v}}(\lambda\sigma\,|\,r)]^{\varkappa_{qkh}(\lambda\sigma|r)}$$

$$\delta\varepsilon_{kh}^{ij}(\lambda\sigma\,|\,r) = \varepsilon_{kh}^{ij*}(\lambda\sigma\,|\,r) - \varepsilon_{kh}^{if}(\lambda\sigma\,|\,r);$$

$$\varkappa_{kqh}(\lambda\sigma\,|\,r) = z_{kh}(\lambda\sigma\,|\,r) - \Delta_{qh}(\lambda\sigma) \tag{20}$$

where $z_{kq}(\lambda\sigma\,|r)$ is the number of sites of the sub-lattice in the layer q at a distance r from a site in the sub-lattice λ in the layer k; $\Delta_{qh}(\lambda\sigma)$ is the Kronecker symbol, equal to 1 for $q = h$ and $\lambda = \sigma$, and equal to 0 in other cases; $\theta_{kq}^{ij}(\sigma\lambda)$ is the probability of finding the particles i and j in the layers k and q in the sub-lattices λ and σ; the parameter of the interaction between i and j is denoted by $\varepsilon_{kq}^{ij}(\lambda\sigma\,|\,r)$. If the layers being considered correspond to a uniform volume, then the indices k and q can be omitted, but in the surface regions the layer number is important. In Eqn.(20), account is taken of the paired interactions with all neighbours situated within R coordination spheres, whose centres are the particles i and v (if the neighbours are situated in the layers $k \pm k_R$ and $q \pm k_R$ respectively). The quantity k_R differs from R, since the distance between neighbouring coordination spheres r and $r + 1$ does not exceed the

distance between neighbouring layers. For example, for a volume lattice with $z = 6$ with $R = 2$, the quantity $k_2 = 1$, as with $R = 1$ and $R = 3$; the distances between the particles, corresponding to $R = 1$, 2, and 3, are a, $a\sqrt{2}$, and $a\sqrt{3}$ respectively. The quantity $k_R = 2$ only for $R = 4$, when the distance between the particles is $2a$. An analogous situation is observed for any other structure.

Thus for a fixed layer number h, the product is taken over all the sites in the layer at different distances from the central particle. In the general case, these sites may belong to different sub-lattices. They must be distinguished in explicit form, since this determines the type of particles s_σ over which the summation in the functions $S^i_{kh}(\lambda\sigma \mid r)$ is carried out. The structure of the solid determines unambiguously the type σ of the sub-lattice in the layer h at a distance r from a site of type λ in the layer k. The parameter of the interaction of the activated complex, formed from a particle i in a site of the sub-lattice δ of the layer k and a neighbouring particle j situated at a distance r in a site of the sub-lattice σ in the layer h, is denoted by $\varepsilon^{ij*}_{kh}(\lambda\sigma \mid r)$; k_{iv} is the pre-exponential factor of the migration rate constant. Eqn.(20) differs from the analogous expression given in Ref.90 in that it takes account of the independent influence of each neighbouring particle j on the central particles i and v.

Eqns.(19) must be supplemented by equations for the functions $\theta^{ij}_{kh}(\lambda\sigma \mid r)$. In the general case it is necessary to examine all pairs of particles in different sub-lattices (in the interstice sub-lattices, the substitution sub-lattices, and pairs of a mixed type containing a particle in the interstice sub-lattice and an atom in the substitution sub-lattice), since they are all taken into account in the functions $S^i_{kh}(\lambda\sigma \mid r)$. These equations have the following general structure:[90]

$$\dot{\theta}^{ij}_{kq}(\lambda\sigma \mid r) = -\sum_h \varkappa_{kqh}(\lambda\sigma \mid r)\,[V^{\overline{vij}}_{hkq}(\lambda\lambda\sigma \mid r) - V^{\overline{iv}j}_{hkq}(\lambda\lambda\sigma \mid r)] - \\ -\sum_h \varkappa_{qkh}(\sigma\lambda \mid r)\,[V^{\overline{iv}}_{kqh}(\lambda\sigma\sigma \mid r) - V^{\overline{vi}}_{kqh}(\lambda\sigma\sigma \mid r)] \qquad (21)$$

In the first summation, the sites h denote adjacent sites of the sub-lattice λ, corresponding to the first index λ in the argument of the term, $\lambda = \gamma, \delta$; in the second summation, h denotes adjacent sites of the sub-lattice δ, corresponding to the last index in the argument of the term. The particles taking part in the elementary process are indicated by a bar above the symbol. The terms of Eqns.(21) are defined by the equations:

$$V^{\overline{ij}}_{hkq}(\lambda\lambda\sigma \mid r) = V^{vi}_{ik}(\lambda\lambda)\,\psi^{ij}_{kq}(\lambda\sigma \mid r)\,\psi^{ij}_{kq}(\lambda\sigma \mid r)\,\psi^{vj}_{hq}(\lambda\sigma \mid r), \\ \psi^{ij}_{kq}(\lambda\sigma \mid r) = \theta^{ij}_{kq}(\lambda\sigma \mid r)\exp[\beta\delta\varepsilon^{ij}_{kq}(\lambda\sigma \mid r)]/[\theta^i_k S^i_{kq}(\lambda\sigma \mid r)] \qquad (22)$$

The normalisation relationships have the form:

$$\sum_{j=1}^{s_\sigma} \theta^{ij}_{kq}(\lambda\sigma \mid r) = \theta^i_k(\lambda);\quad \sum_{l=1}^{s_\lambda} \theta^{ij}_{kq}(\lambda\sigma \mid r) = \theta^j_q(\sigma);\quad \sum_{i=1}^{s_\lambda} \theta^i_\alpha(\lambda) = 1 \qquad (23)$$

With allowance for these relationships, the system of equations (19)–(23) is closed, and it can be solved by specifying the initial and boundary conditions.

The above equations are readily generalised by taking account of the real characteristics of different systems in the following cases: 1) when the number of interstices does not coincide with the number of sites in the substitution lattice (for example for tetrahedral interstices in a FCC lattice); 2) when the migration of the particles of the substance diffusing takes place through interstices of different types and (or) the alloy is in an ordered state; and 3) when there is an additional displacement of the particles of different sub-lattices; in this case the atoms of the alloy move into the interstices and migrate in them, and the particles of the substance diffusing occupy vacancies in the substitution lattice.

From these equations under quasi-equilibrium conditions for individual sub-systems (sub-lattices) it is possible to obtain equations describing the distribution of the particles of the substance diffusing in different phase states (phase transformations involving ordering and separation into layers or any one of these may take place), as in Ref.55, where the analysis was carried out in the molecular field approximation. In this approximation, there are no effects of correlation of interacting particles. The question of taking account of correlation effects is central in kinetic studies. They may lead to qualitative changes in the description of the kinetic characteristics of a system.[63]

V. VITREOUS INORGANIC AND POLYMERIC MEMBRANES

The molecular models of the transfer of substances in crystalline membranes, described above, are capable of reflecting many important aspects of transfer processes in vitreous membranes. This also applies to silicate glasses[91,92] and to vitreous polymeric membranes. Since the latter are of practical importance, they will be considered in more detail. The available experimental material and an analysis of the trends in the development of transfer models indicate an analogy between the processes taking place in crystalline and vitreous solids. Thus the use of high pressures in a number of gas-separation systems[1,2,93–95] leads to a relatively extensive saturation of the membranes by the diffusing substance. In this case, the appearance of effects of mutual influence is possible. These effects may be due to either the direct interaction of the molecules or an indirect interaction through the polymeric matrix. The substance diffusing may alter the internal state of the polymeric matrix. Relaxation processes also influence the nature of the transfer.[96,97] The elementary processes in glasses, in particular the migration jumps of molecules, and the state of the glasses are inter-related.[98] This makes necessary a combined description of the evolution of the gas–matrix system.

An important role in the transfer of substances in vitreous and crystalline membranes is played by surface processes. A change in the properties of the surface alters its adsorption properties and the solubility of gases in the bulk of the membrane. The latter has a marked influence on the degree of non-equilibrium character of the mass-transfer conditions.[99–101] Thus the surface modification of polymeric membranes based on block copolymers of an arylene sulphoxide with dimethylsiloxane produces a marked change in their gas-permeability with respect to O_2, CO_2, and N_2.[102] The role of the surface in the processes involved in the transfer of ions through polymeric membranes was examined in Refs.103 and 104.

The state of a surface can be described using the multi-layer surface region scheme examined above. The main problem is the relationship between the migration processes and the evolution of the states of the glass. In Ref.98 this problem was solved by changing to the problem of the evolution of the Ising systems: the state of a given elementary volume is characterised by its "internal" energy and the energy of its interaction with a neighbouring elementary volume (the elementary volumes form a lattice in the bulk of the glass). In each elementary volume there is a set of discrete energy minima. The transitions between different energy states of the elementary volume are described by the equations of Glauber.[105,106] They are closed using the molecular field approximation.

The equations given in the previous section are also Glauber equations, but they were closed using a more accurate approximation taking account of short-range correlation effects. They can be used to obtain a description of vitreous systems if each discrete state of the elementary volume [98] is related to atoms of a definite type in the alloy. A more detailed description of the states of glasses is also possible, however, if a particular direction is distinguished in the volume and the group of possible states of the fragments of the polymer (or silicate) chain is examined relative to this direction. A change in the relative orientation of neighbouring fragments of the chains takes place either as a result of internal rotation within a given fragment or cooperatively as a result of conformational rearrangements of several fragments.[107-110] The transitions between different states are associated with the overcoming of corresponding activation barriers.

This formulation of the problem makes it possible to solve a wide range of problems associated with the transfer of substances through vitreous membranes.

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Problems related to the present state of the molecular-kinetic theory of transfer processes in solid crystalline and vitreous membranes, based on the use of information on the interactions between the particles, have been examined. The energy parameters are divided into two groups, characterising the interaction of the particles in the ground and transition states. The expressions proposed for the rates of the reactions in the forward and back directions for each stage of the process are consistent with the description of the equilibrium distribution of the particles.[59,88] This makes it possible to determine the parameters of the interaction of the particles in the ground state on the basis of independent measurements of the thermodynamic characteristics (for example the heats of adsorption and absorption, the isotherms of these processes, equilibrium diagrams, etc.).

A characteristic feature of the models taking account of the restricted mobility of the components of a solid is the existence of kinetic equations which describe the changes in the concentrations of different pairs of particles, and this makes it possible not only to characterise the evolution of local compositions but also to estimate the relative arrangement of the components, that is it makes it possible to obtain the details of the membrane structure and to describe its rearrangement. This in turn makes it possible to raise the question of the influence of the method of preparation of the membranes on their permeability.

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