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FP2 Phenomenological theory of the facilitated diffusion of gases in fixed site carrier membranes at non-steady state

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**Abstract**

A generalized phenomenological theory is given for the facilitated transport of gases at the nonsteady state. A dissociative diffusion transport model with a reversible and nonreversible chemical reaction of the first and the second order is used to describe various possible transport mechanisms.

**Introduction**

One of the strategies considered to develop new highly-selective and highly-permeable membranes for gas separation is to create so-called fixed-site carrier (FSC) membranes. Such membranes are very selective because of the specific reversible chemical reactions which take place between certain gas components and membrane reactive sites; the latter are chemically bound to the polymeric matrix and do not diffuse through the membrane, in comparison to the conventional immobilized liquid membranes (ILM).

The mechanism of the highly-selective facilitated-transport (FT) of a certain gas component through such FSC membranes was referred to as the so-called "Tarzan swing" mechanism (Cussler et al 1989). This mechanism requires the existence of a percolation threshold, below which no facilitated transport will take place. Another approach describing the FT mechanism uses a dual-model transport model to describe facilitated diffusion in membranes (Noble 1992). Both these mechanisms were applicable for steady-state diffusion. A main feature of this theory was the derivation of the so-called effective diffusion coefficient, in terms of morphology-dependent and reversible reaction variables.

Results of the nonsteady-state diffusion experiments, in terms of the effective diffusion coefficient, are not easily described. Since the effective diffusion coefficient depends on several variables, including experimental conditions (for example, partial pressure) and time of experiment, the steady-state gas-permeation experiments are not adequately informative to determine, for example, reaction parameters of the reversible complexation, which takes place in such membranes. The presence of the reactive fixed sites in the membrane also leads to changes in the shape of the kinetic permeability curves. For example, in the case of a homogeneous nonreactive membrane all values of the diffusion coefficient, calculated from the so-called "particular points" on a permeability kinetic curve obtained by means of different gas-permeation experimental techniques (integral permeability method, differential, impulse and differential impulse methods), are identical (Beckman 1991).

For nonhomogeneous membranes where reactive fixed sites lead to enhanced diffusion and to short diffusion times, the values of the diffusion coefficient calculated from these "points" differ. Investigation of the principles of nonsteady-state gas transport in such membranes is therefore of both fundamental and industrial interest.

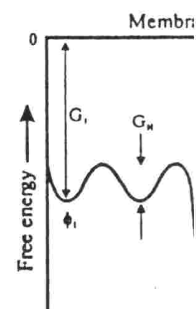


Figure 1. Passive sites ( $\phi_2$ ).  $G_1$  is a free energy of a transition state.  $G_2$  is a free energy of a transition state.  $G_H$  is a free energy of a hop between passive sites.

membrane with two solute diffusion streams, so formally be considered as a universal model for gas separation membranes for gas separation. Model assumption which are able to react and releasing a solute from the morphology of the potential wells with movements through categories according

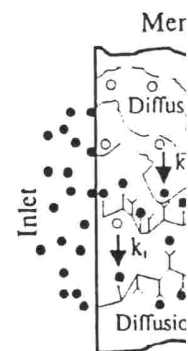


Figure 2. Schematic dissociative diffusion.

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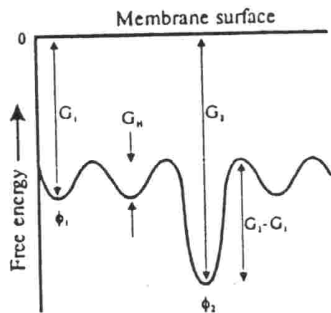


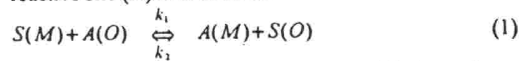
Figure 1. Passive sites ( $\phi_1$ ) and reactive sites ( $\phi_2$ ).  $G_1$  is a free energy (FE) of a passive site.  $G_2$  is a FE of a reactive site.  $G_H$  is a FE of a hopping between passive sites.

It is to be noted here, that, more than 35 years ago, solid-state physics faced the problem of explaining the rapid diffusion of certain metals (for example, copper) in other metals (for example, in germanium) (Frank et al 1956, Wei 1961). Later the problem of explaining some anomalies of hydrogen diffusion in metals was raised (McNabb et al 1963, Oriani 1970). In order to explain these experimental facts, the modified second order diffusion equation (Fick's equation) was introduced and treated in various ways (Boctor et al 1976, Schroeder 1976, Frank et al 1979, Yoshida et al 1971, Kupriazhkin et al 1979, Beckman 1988, 1994).

This conception was based on the assumptions that atoms, diffusing in solids, are often trapped by lattice imperfections such as vacancies, voids, dislocations and other interstitial impurities, making it possible to introduce two (or more) diffusion channels. One of these diffusion models considers the transport of a molecule through a membrane with two diffusion coefficients:  $D_1$  and  $D_2$ . The diffusion coefficient  $D_1$  relates to the simple solute diffusion. The diffusion coefficient  $D_2$  is defined in terms of the diffusion of molecules in fixed sites in the membrane. When a molecule, diffusing in a membrane, is exchanged between two diffusion streams, so-called dissociative diffusion takes place. Since trapping and releasing rates can formally be considered as reversible chemical reaction rates, the dissociative diffusion model (DDM) may be a universal mathematical concept by which to treat facilitated diffusion in fixed-site carrier membranes for gas separation.

**Model assumptions** The process of gas diffusion in a membrane comprising reactive fixed sites which are able to react with gas molecules is considered. It is assumed that the probability of holding and releasing of a solute molecule by reactive sites are independent of time. It is supposed here that the morphology of the membrane sample can be described by a uniformly distributed population of potential wells with varying capacities for capturing and delaying gas molecules on their random movements through the membrane. It is further supposed that these traps can be divided into two categories according to the tenacity with which they hold a captured molecule. Those in the first category are "passive" sites, having a negligible capturing effect, while those in the second category are deep potential wells, i.e. chemically "active" sites (Figure 1). These two types of potential wells are characterized by two values of Gibbs' free energy:  $G_1$  and  $G_2$ , respectively.

The diffusion coefficient  $D_1$  relates to the simple solute diffusion through "passive" sites. The diffusion coefficient  $D_2$  is defined in terms of the diffusion of molecules in fixed sites in the membrane (Figure 2). It is assumed that the chemical reaction between solute molecule (M) and reactive site (A) is as follows:



where  $S(M)$  is the gas molecule dissolved in the polymeric matrix (state  $\phi_1$ );  $S(O)$  is the vacant site in the polymeric matrix that is able to dissolve the gas molecule;  $A(O)$  is the reactive fixed-site;  $A(M)$  is the complex between the

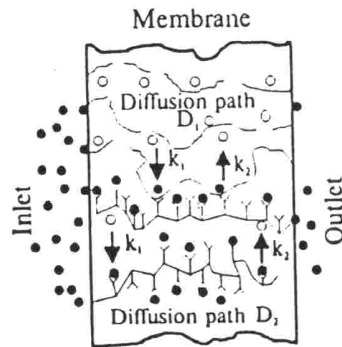


Figure 2. Schematic diagram of the dissociative diffusion mechanism

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gas molecule and the reactive site (state  $\phi_2$ );  $k_1$  and  $k_2$  are the rate constants of the exchange type of  $\phi_1 \rightarrow \phi_2$  and  $\phi_2 \rightarrow \phi_1$ , respectively. The equilibrium reaction constant for the process (1) is as follows:

$$K = \frac{k_1}{k_2} = \frac{C_2(C_S - C_1)}{C_1(C_A - C_2)}, \text{ where } C_1 = n_1/V \text{ and } C_2 = n_2/V \text{ are the concentrations of the gas}$$

molecules in dissolved form and in the complex form with reactive sites in state  $\phi_1$  and  $\phi_2$ , respectively;  $n_1$  and  $n_2$  are the numbers of the molecules in state  $\phi_1$  and  $\phi_2$ , respectively ( $n_1 + n_2 = n$ ).  $V$  is the volume of membrane sample.  $C_S$  and  $C_A$  are the concentrations of the vacant sites for molecules to be dissolved in the polymer and molecules to form complexes with reactive sites, respectively.

The system of the differential equations, describing one-dimension diffusion in a planar membrane with a thickness  $l$ , when a chemical reaction takes place between gas molecules and reactive sites, is given by the following differential equations:

$$\begin{aligned} \frac{\partial C_1}{\partial t} &= \frac{\partial}{\partial x} \left[ D_1(x, C, t) \frac{\partial C_1}{\partial x} \right] - k_1 C_1 (C_A - C_2) + k_2 C_2 (C_S - C_1) \\ \frac{\partial C_2}{\partial t} &= \frac{\partial}{\partial x} \left[ D_2(x, C, t) \frac{\partial C_2}{\partial x} \right] + k_1 C_1 (C_A - C_2) - k_2 C_2 (C_S - C_1) \end{aligned} \quad (2 \text{ a,b})$$

#### Mathematical problem and analytical solution

In the absence of local equilibrium the system of the differential equations (2 a,b) should be solved using the following general initial and boundary conditions:

Initial conditions: (3)

$$C_1(x, 0) = C_{10}(x); \quad C_2(x, 0) = C_{20}(x)$$

Boundary conditions:

$$C_1(0, t) = \varphi_1(t); \quad C_1(l, t) = \varphi_2(t); \quad C_2(0, t) = \Phi_1(t); \quad \text{and} \quad C_2(l, t) = \Phi_2(t) \quad (4)$$

The above boundary conditions take into consideration possible concentration changes at the boundary of the membrane with time. The system of the differential equations (2 a,b) is nonlinear and, therefore, does not have an analytical solution. All consequences of the model presented nevertheless can be solved analytically, provided that the diffusion coefficients  $D_1$  and  $D_2$  are constants.

#### Examples

**A: Dissociative diffusion and reversible chemical reaction of the first order.** If the concentration of both types of traps are considerably larger than the concentration of the gas molecules, dissolved in the membrane and distributed among both types of the traps, then it is reasonable to consider the new constants:  $k_1^* = k_1 C_A$  and  $k_2^* = k_2 C_S$ . In this case system (2) is reduced to a linear system of the differential equations. Such a system is solved by means of Fourier transforms with initial (3) and boundary conditions (4).

**B: One-channel diffusion with trapping.** If  $D_2 = 0$ , the system of differential equations (5 a,b) should be solved:

$$\frac{\partial C_1}{\partial t} = D_1 \frac{\partial^2 C_1}{\partial x^2} - k_1^* C_1 + k_2^* C_2 \quad (5 \text{ a,b})$$

$\frac{\partial C_2}{\partial t} = k_1^* C_1 - k_2^* C_2$   
The nonsteady-state solution of system (5) was obtained by means of Laplace transforms.

#### Results and conclusions

The above-mentioned diffusion models are linear and, therefore, permit obtaining the analytical solutions. The use of arbitrary initial and boundary conditions allows application of this general theory for the mathematical treatment of various diffusion experiments. The analytical solutions of various models can be very useful and an effective asymptotic approximation for the assessment of numerical

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calculations. Equations presented here allow for the mathematical treatment and interpretation of nonsteady-state diffusion experiments to be performed. A full analytical solution of the problem allows the permeability curve to be analyzed and the reaction kinetic parameters to be obtained. By means of computer simulation the influence of the reactive-sites on a kinetic permeability curve was studied in terms of abovementioned models. As a result of this study the analytical equations describing nonsteady-state concentration profiles, nonsteady-state fluxes, four main statistical parameters of various permeability curves, etc were obtained.

It is reasonable that the phenomenological theory presented can be expected to be a basic approach for describing nonsteady-state separation processes in hybrid liquid-membrane systems and reactors (Beckman et al 1993, Bessarabov et al 1995 (a,b)).

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