Computer Modeling of the Nonstationary State of Saturation of A Membrane in the Form of Taking Into Account Relaxation Times

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Abstract. The paper reviews a model is developed for the nonstationary state of saturation of a membrane. In the main part of the paper, transfer equations with cross effects such as the Soret effect and thermal diffusion are derived. On the basis of these equations, cross effects, heat transfer and mass transfer equations in the conjugate form are obtained. As a result, equations are obtained for component fluxes in the transition period, taking into account the relaxation time, where the aspect of membrane nonstationarity is associated with transient processes in establishing the state of stationary saturation of the membrane. Moreover, it was shown that the concentration of the dissolved substance near the membrane does not exceed the equilibrium concentration, which avoids clogging of pores with polymeric molecules. However, the apparent separate porosities for the dissolved component and the solvent in the "slip" porosity zone depend on the saturation of the membrane pores by the filtering components. All this is described in the discussions of the paper. In the results, the computer model of non-stationary saturation of the membrane with the application of the Chemkad application program allowed to obtain graphs of the dependence of the non-stationary saturation state of the membrane on various gases in the porosity zone, in particular, gases such as ethanol and methane are considered.

1. Introduction
Numerous phenomena of diffusion, mass transfer and migration vary significantly from a physical point of view, but can be described by a single mathematical apparatus. This apparatus has a complex nature, including such directions as the statistics of forced or random walks, the phenomenological description of diffusion by partial differential equations and elements of nonequilibrium thermodynamics.

The mathematical apparatus of diffusion is quite complex, it is not inferior in complexity to the apparatus of quantum mechanics, and in some cases exceeds it. Diffusion uses statistical distributions that do not have finite variance and higher moments. Some equations have no solution at all.

In practice, the analogy between diffusion and thermal conductivity is often used. Mathematically, Fick's laws are analogous to the equations of Fourier thermal conductivity. This analogy is based on the general patterns of irreversible processes of redistribution of the intensive parameters of the state
(concentration, temperature, pressure, etc.) between different parts of a system as it tends to thermodynamic equilibrium. [1]

In traditional membrane technology, a mixture of gases is separated only from stationary conditions. The partition factor is defined as \( \alpha_{ss} = P_A / P_B \). Under stationary conditions, by definition, a mixture of gases A and B for which \( P_A = P_B \) cannot be separated.

However, such a mixture can be separated if the separation is conducted in the non-stationary permeability mode. In this case, it is necessary to take into account both the relaxation times of the thermal and diffusion phenomena.

Therefore, it should be written transfer equations with cross effects such as the Soret effect and thermal diffusion.[2]

2. The Main Part
In order to take into account to cross effects, the heat transfer and mass transfer equations must be written in conjugated form. It can be done as follows:

\[
\frac{\partial N_m}{\partial t} = -N_m \tau_m^{-1} + N_h \tau_x^{-1} 
\]

\[
\frac{\partial N_h}{\partial t} = -N_m \tau_x^{-1} + N_h \tau_h^{-1} 
\]

Herewith, \( \tau_x \) can be determined as the perturbation time by analogy with the relaxation time. The indexes \( m \) and \( h \) mean mass and heat, respectively.[3] And it is important that in the quasiequilibrium approximation of the system the condition for the damping of perturbations be fulfilled [4]:

\[
\tau_x > \sqrt{\tau_m \tau_h} 
\]

The obtained solutions show that the first terms in the equations are related to the direct flows, and the second ones are the flows associated with the cross flows. [5] Then the expressions for the corresponding relaxation kernels of transfer are obtained in the forms [6]:

\[
N_{nm} = \frac{\eta_m}{\lambda_2 - \lambda_1} \left[ \left( \lambda_2 + \frac{1}{\tau_m} \right) \exp(\lambda_1 s) - \left( \lambda_1 + \frac{1}{\tau_m} \right) \exp(\lambda_2 s) \right] 
\]

\[
N_{hh} = \frac{\eta_h}{\lambda_2 - \lambda_1} \left[ \left( \lambda_2 + \frac{1}{\tau_h} \right) \exp(\lambda_1 s) - \left( \lambda_1 + \frac{1}{\tau_h} \right) \exp(\lambda_2 s) \right] 
\]

\[
N_{mh} = N_{hm} = \frac{\eta_x}{\tau_x (\lambda_2 - \lambda_1)} \left[ \exp(\lambda_1 s) - \exp(\lambda_2 s) \right] 
\]

Since the fluxes of both components in a two-component system are linearly interrelated and, taking into account the low concentration of the diffusing impurity,[7] we can adopt the following expressions of the fluxes:
\[
J_m = \int_0^t N_{mm} f \nabla \nu(R, t_1) dt_1 + \int_0^t N_{mh} \nabla \beta(R, t_1) dt_1
\]  

(7)

\[
J_h = \int_0^t N_{hm} f \nabla \nu(R, t_1) dt_1 + \int_0^t N_{hh} \nabla \beta(R, t_1) dt_1
\]  

(8)

Hence the equations for the streams take the form:

\[
\frac{\partial^2 J_m}{\partial t^2} = (D_{1-2}) \frac{\partial J_m}{\partial t} - D_{12} J_m - \eta_m \beta \nabla v \left( C + \frac{1}{\tau_m} \right) + \eta_x \nabla \beta + \eta_m \frac{\partial}{\partial t} (f \nabla v)
\]  

(9)

\[
\frac{\partial^2 J_h}{\partial t^2} = D_{1-2} \frac{\partial J_h}{\partial t} - D_{12} J_h - \eta_h \nabla \beta \left( C + \frac{1}{\tau_h} \right) + \eta_x \beta \nabla v + \eta_h \frac{\partial}{\partial t} (f \nabla \beta)
\]  

(10)

The laws [8] of conservation of mass and energy can be written as:

\[
\frac{\partial \hat{c}}{\partial t} + \nabla J_m = 0
\]  

(11)

\[
\frac{\partial \hat{e}}{\partial t} + \nabla J_h = 0
\]  

(12)

As a result, the transfer equations become:

\[
\frac{\partial^3 c}{\partial t^3} - \left( \frac{1}{\tau_m} + \frac{1}{\tau_h} \right) \frac{\partial^2 c}{\partial t^2} + \left( \frac{1}{\tau_m \tau_h} - \frac{1}{\tau_x} \right) \frac{\partial c}{\partial t} + \eta_m \nabla (f \nabla v) + \frac{\eta_x}{\tau_x} \Delta \beta + \eta_m \frac{\partial}{\partial t} (f \nabla v) = 0
\]  

(13)

\[
\frac{\partial^3 e}{\partial t^3} - \left( \frac{1}{\tau_m} + \frac{1}{\tau_h} \right) \frac{\partial^2 e}{\partial t^2} + \left( \frac{1}{\tau_m \tau_h} - \frac{1}{\tau_x} \right) \frac{\partial e}{\partial t} + \eta_h \nabla \beta + \frac{\eta_x}{\tau_x} \Delta \beta + \eta_h \frac{\partial}{\partial t} (\Delta \beta) = 0
\]  

(14)

3. Discussion
Consequently, the aspect of membrane nonstationary is associated with transient processes of establishing the state of stationary saturation of the membrane. [9]

The apparent separate porosities for the dissolved component and the solvent in the "slip" porosity zones to depend on the saturation of the membrane pores by the filtering components and, accordingly,

\[
\hat{e}_1 = \hat{c} S_1, \quad \hat{e}_2 = \hat{c} S_2,
\]  

(15)

Where, as a hypothesis, it can be assumed that for an unsteady process at any time, an equality similar to that for a stationary process is observed:

\[
S_1 + S_2 = \frac{\hat{c} P'}{\hat{e}}
\]  

(16)

With steady-state ultrafiltration in the flow regime, no dissolved component is accumulated in the membrane in the "slip" stream filtration zone. [10] This condition is written as:
\[ C_p = \frac{V_2}{V_1 + V_2} = f(z) \]  
\[ \frac{\partial C_p}{\partial y} = 0 \]  

In the transition period, we can approximate the function \( C_p(t) \) as:
\[ \frac{\partial C_p}{\partial t} = \frac{\partial}{\partial t} \left( \frac{V_2}{V_1 + V_2} \right) = f(z,t) \]  

Furthermore
\[ J_p = \frac{C_p V_1}{1 - C_p} \]  
\[ \varepsilon_S = 1 - \varepsilon_p \]  

### 4. Results

Thus, we have obtained a nonlocal description of the separation process, taking into account the long-term effects of memorization in the system of globules and the non-commutability of the system.\[11\] The drift intensity at times steps depend on the history of the process and is determined by the kinetic characteristics at all preceding moments \( \tau_i \leq \tau \).\[12\]

Figure 1 shows a characteristic form of the dynamics of the cross component of the relaxation transfer nucleus.

Moreover, the effective diffusion coefficient changes with time when the structure of the kinetic zones changes during the flow of the mixture through the membrane.\[13\]

The model predicts an increase in the effective diffusion coefficient in time and the displacement of the fractal zone in the membrane.

Applying a package of Chemcad application programs, we get the following dependency curves for ethanol and methane at the porosity zone (Figure 2, Figure 3).
Library Ideal Gas Heat Capacity. Ethanol

![Diagram for the Ethanol component](image1)

**Figure 2.** Diagram for the Ethanol component

Library Ideal Gas Heat Capacity. Methane

![Diagram for the Methane component](image2)

**Figure 3.** Diagram for the Methane component
5. Conclusion

Only the solvent moves through this channel system. Moreover, supposing that the concentration of the dissolved substance near the membrane does not exceed the equilibrium concentration, clogging of the pores with polymer molecules does not occur.

Based on this model, we obtain equations for the flow of components in the transition period.

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