DISTRIBUTION OF GAS MIXTURES ON FINE-PORE MEMBRANES UNDER NONISOTHERMAL CONDITIONS

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The separation of gas mixtures on fine-pore membranes is analyzed with allowance for interphase effects, which occur during the nonisothermal flow of a gas in pores.

Borman et al. [1-3] have made a theoretical study of mass transport under nonisothermal conditions in pores, whose diameter is smaller than the phonon mean free path of a solid. In this case the transport equation contains an additional term, which is proportional to the temperature gradient in the solid, depends on the temperature and channel diameter, but is independent of the molecular mass. This term is due to the interaction of gas molecules and phonons of the nonequilibrium solid. Depending on the direction of the gas-density and temperature gradients, the gas flow through a pore can either increase while simultaneously the mixture separation factor decreases or, conversely, the separation factor increases while the flow decreases.

Here we propose a mathematical model and report the result of computational modeling of gas separation on fine-pore membranes under nonisothermal conditions for the case when allowance must be made for the interphase effect of the interaction of gas molecules with phonons of a nonequilibrium solid.

Let us consider a flat fine-pore membrane (Fig. 1). The initial gas mixture (consisting of N components with relative molar concentrations x_i ($i = 1, ..., N$)) in the high-pressure chamber (HPC) at temperature T_1 and pressure P_1 penetrates in the free-molecule mode through pores of the membrane into the low-pressure chamber (LPC), where the relative molar concentrations of the components of the gas mixture are x_i'($i = 1,..., N$) and the temperature and pressure are T_2 and P_2, respectively.

We shall assume that surface diffusion has a negligible effect on the flow of the gas mixture in the pores of the membrane and the accommodation coefficient is equal to 1.

Borman et al. [3] obtained an expression for the average velocity (over the pore cross section) of the i-th component of the mixture

$$\mathbf{u}_i = -\frac{a_i\bar{V}_i d}{2}\left(\frac{\nabla\rho_i}{\rho_i} + \frac{\nabla T}{2T}\right) - c_i\bar{V}_i\lambda_F\frac{\nabla T}{T},\quad i = 1,\ ...,\ N, \tag{1}$$

and showed that the second term in this expression for light gases does not depend on the molar mass of the i-th component and has the same value for all components of the mixture.

Using (1), we can write an expression for the flux density of the i-th component, penetrating through the membrane, in the form

$$j_i = -\frac{\varepsilon a_i\bar{V}_i\bar{d}}{2\xi R\sqrt{T}}\frac{d(p_iT^{-1/2})}{dz} - \frac{\varepsilon c_i\bar{V}_i\lambda_F p_i}{\xi RT^2}\frac{dT}{dz},\quad i = 1,\ ...,\ N. \tag{2}$$

The first term on the right side of Eq. (2) is the flux density of the i-th component of the mixture and is due to the existence of pressure and temperature gradients [4]. The second term is proportional to only the temperature gradient. This term makes allowance for the effect that the drag on gas molecules by phonons of the membranes has on the flux j_i.

We write j_i in terms of the given P_1, T_1, P_2, T_2. For this purpose we integrate (2) over the thickness of the membrane from 0 to δ. We confine the discussion to light gases. Since the product $c_i\lambda_F$ at $T \sim 300$ K depends weakly on the temperature, for simplicity we assume that $c_i\lambda_F$ is independent of T. Moreover, we replace the pressure p_i in the second term of Eq. (20) by the average partial pressure of the i-th component $(p_{1i} + p_{2i})/2$. We also note that although

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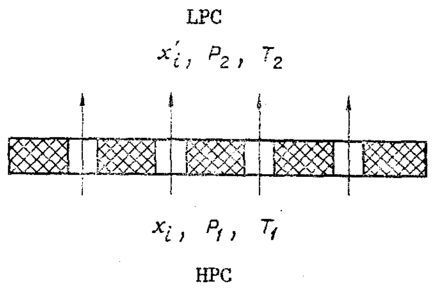

Fig. 1. Diagram of organization of the process.

the flux density j_i is a function of z, the flow of the i-th component of the mixture penetrating through the membrane does not depend on the coordinate z, on the assumption that the system consisting of gas and pore wall is in local equilibrium.

Integrating (2) with allowance for these assumptions, we obtain an expression for the flux density of the i-th component of the mixture penetrating through the membrane:

$$J_i = \frac{\varepsilon a_i \overline{V}_{1i} \overline{d}}{2\xi R T_1 \delta}\left(p_{1i} - p_{2i}\sqrt{\frac{T_1}{T_2}}\right) + \\ + \frac{\varepsilon c_i \overline{V}_{1i} \lambda_F}{\xi R T_1 \delta}(p_{1i} + p_{2i})\left(\sqrt{\frac{T_1}{T_2}} - 1\right), \quad i = 1, \ldots, N. \tag{3}$$

Denoting $Q_i = \varepsilon a_i \overline{V}_{1i} \overline{d}/(2\xi R T_1)$, with allowance for the obvious equalities $x_i = p_{1i}/P_1$ and $x_i' = p_{2i}/P_2$ we recast (3) in the final form

$$J_i = \frac{Q_i^* P_1}{\delta}(x_i - \gamma_i^* x_i'), \quad i = 1, \ldots, N, \tag{4}$$

where

$$Q_i^* = Q_i\left(1 + k_i^F\left(\sqrt{\frac{T_1}{T_2}} - 1\right)\right), \tag{5}$$

$$\gamma_i^* = \gamma\left(\sqrt{\frac{T_1}{T_2}} - k_i^F\left(\sqrt{\frac{T_1}{T_2}} - 1\right)\right)\bigg/\left(1 + k_i^F\left(\sqrt{\frac{T_1}{T_2}} - 1\right)\right), \tag{6}$$

$$k_i^F = 2c_i\lambda_F/(a_i\overline{d}), \quad i = 1, \ldots, N, \quad \gamma = P_2/P_1.$$

We note that as $k_i^F \rightarrow 0$ formula (3) goes over into the familiar formula [5] for the gas flux density through a porous membrane, when pressure and temperature drops exist at the ends of the pores. The ratio of coefficients k_i^F and k_j^F ($i \neq j$) is proportional to $\sqrt{m_i/m_j}$, since coefficients c_i and c_j are proportional to $\sqrt{m_i}$ and $\sqrt{m_j}$, respectively, and coefficients a_i and a_j differ insignificantly, as a rule.

Since the composition of the mixture in the HPC is constant, the concentration x_i' in the LPC appearing in (4) can be calculated from a formula similar to that given in [6]:

$$x_i' = \frac{Q_i^* x_i}{\gamma_i^* Q_i^* + \sum_{k=1}^{N} Q_k^*(x_k - \gamma_k^* x_k')}. \tag{7}$$

Let us analyze Eq. (4) at different values of $\sqrt{T_1/T_2}$ for a binary gas mixtures, assuming that the components are numbered in order of increasing molar mass.

When $\sqrt{T_1/T_2}$ ($\sqrt{T_1/T_2} > 1$) increase at not very large temperature differences the effective permeability coefficients Q_1^* and Q_2^* increase and γ_1^* and γ_2^* decrease in comparison with the same quantities in the absence of a temperature drop in the membrane. As a result, on the one hand, the membrane output in respect to the penetrating gas flow increases and, on the other hand, its selective properties diminish.

A decrease in $\sqrt{T_1/T_2}$ on condition that $\sqrt{T_1/T_2} < 1$, as is seen from (5), causes an increase in Q_1^* and, therefore, in the membrane output along with a simultaneous increase in the selectively. It follows from (6) that γ_i^* will also increase. Several cases can be observed, depending on the process parameters.

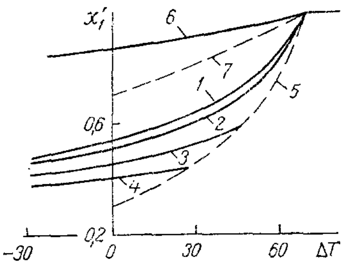

Fig. 2

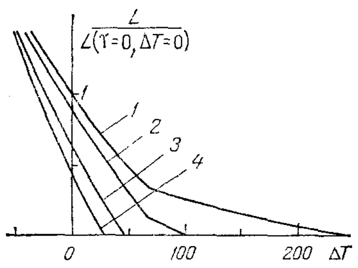

Fig. 3

Fig. 2. Helium concentration x_1' in gas flow penetrating through a porous membrane as a function of the temperature drop ΔT(K); $x_1 = 0.3$: 1) $\gamma = 0$, 2) 0.1, 3) 0.2, 4) 0.4; 5) $x_1' = x_1/\gamma_1^*$; $x_1 = 0.7$: 6) $\gamma = 0$; 7) $x_1' = x_1/\gamma_1^*$.
Fig. 3. Relative membrane output with respect to penetrating gas as a function of the temperature drop ΔT(K); $x_1 = 0.3$: 1) $\delta = 0$, 2) 0.1, 3) 0.2, 4) 0.4.

Let us consider the case when the condition $\gamma_1'^* < x_1$ is satisfied for all value of the temperature satisfying the relation $\sqrt{T_1/T_2} > (k_2^F - 1)/k_2^F$. For any membrane material this condition can be achieved by choosing the value of $\gamma = P_2/P_1$.

From (5) it follows that as $\sqrt{T_1/T_2}$ decreases the quantities Q_i^* decrease, with Q_1^* always greater than Q_2^*. As $\sqrt{T_1/T_2} \to (k_2^F - 1)/k_2^F$ the value of $Q_2^* \to 0$. As a result, virtually only one component begins to penetrate through the membrane and the composition $x_1' \to 1$, $x_2' \to 0$ is established in the LPC. As $\sqrt{T_1/T_2}$ decreases further the permeability of the first component is lowered and $Q_1^* = 0$ at $\sqrt{T_1/T_2} = (k_1^F - 1)/k_1^F$. The condition $\gamma_1^* \leq x_1$ should be satisfied in this case. If $\gamma_1^* \to x_1$ inside the interval $(k_1^F - 1)/k_1^F < \sqrt{T_1/T_2} < (k_2^F - 1)/k_2^F$, then $J_1 \to 0$ in accordance with (4) and the membrane becomes impermeable to the mixture at a temperature gradient corresponding to the conditionn $\gamma_1^* = x_1$.

Suppose now that the condition $\gamma_1^* > x_1$ begins to be satisfied at $\sqrt{T_1/T_2} > (k_2^F - 1)/k_2^F$. In this case the penetration through the membrane is determined not so much by the variation of the permeability Q_i^* as by the increase in γ_1^*. As $\sqrt{T_1/T_2}$ decreases, as already mentioned, the values of γ_1^* grow and the difference $\gamma_2^* - \gamma_1^*$ is always greater than zero and increases in absolute value. Analysis of (4) with allowance for $x_i' = J_i / \sum_{k=1}^{2} J_k$ $(i = 1, 2)$ under these conditions shows that the value of x_1' grows with the temperature gradient and the fluxes of both components decrease. When the value of $\sqrt{T_1/T_2}$ is such that for all i we have

$$x_i = \gamma_i^* x_i', \tag{8}$$

the fluxes of all components through the membrane simultaneously become zero, i.e., the mixture ceases to penetrate and an equilibrium composition is established in the LPC; this composition is determined by the solution of the system of equations

$$x_1' + x_2' = 1, \quad \gamma_1^* x_1' + \gamma_2^* x_2' = 1, \tag{9}$$

where the second equation was obtained by summing (8). The solution (9) for a binary mixture has the form

$$x_1' = \frac{\gamma_2^* - 1}{\gamma_2^* - \gamma_1^*}, \quad x_2' = \frac{1 - \gamma_1^*}{\gamma_2^* - \gamma_1^*}. \tag{10}$$

We can easily prove that the fluxes of the components disappear simultaneously by considering the opposite scenario. Suppose that $J_2 = 0$ and $J_1 > 0$. Then this means that $x_1' = 1$, which cannot occur since at $x_1 < \gamma_1^* x_1'$ we immediately get $J_1 < 0$ from (4).

The functional dependence $x_1' = x_1/\gamma_1^*$ is an equation which describes the locus of points at which the membrane output with respect to the penetrating flow is zero. On the other hand, the formula

$$x_i' = \frac{Q_i^* x_i}{Q_1^* x_1 + Q_2^* x_2}, \quad i = 1,\ 2, \tag{11}$$

gives the values of x_1' at $\gamma = 0$. Equations (10) and (11) determine the range of allowable values of x_1'.

As an example we give the calculation of the parameters of separation of a two-component He—N_2 mixture on a porous membrane of the nuclear filter type with a mean pore diameter $\bar{d}$ ~100 Å and component permeabilities $Q_{He} = 10 \cdot 10^{-12}$ mole/m²·sec·Pa and $Q_{N_2} = 3.7 \cdot 10^{-12}$ mole/m²·sec·Pa. Here and below the subscript i takes on a value of 1 for helium and 2 for nitrogen.

Let us assign the values $P_1 = 9.8 \cdot 10^3$ Pa and $T_1 = 293$ K for the pressure and temperature, respectively, in the HPC. The values of the coefficients k_i^F are difficult to determine. For convenience we set $k_i^F = 3.7$ and $k_2^F = 10.0$, which is close to the theoretical estimates for polymer membranes [3]. The calculations were carried out for different concentrations of the components in the mixture and the values of the gas pressure and temperature in the LPC.

Figure 2 shows the curves of the helium concentration x_1' versus the temperature drop at the membrane $\Delta T = T_2 - T_1$. The regions of possible compositions of mixture in the LPC are contained between curves 1 and 5 for $x_1 = 0.3$ and curves 6 and 7 for $x_1 = 0.7$. The points of intersection of the curves with the ordinate axis ($\Delta T = 0$) correspond to Knudsen separation in the isothermal case for different values of γ. Curves 3 and 4 end at the point of intersection with curve 5, which was plotted for the case when $x_1' = x_1/\gamma_1^*$. The equilibrium composition of the mixture at these points is determined from (10). The points of intersection of curves 1, 2 with 5 and curve 6 with 7 correspond to the point $Q_2^* = 0$.

Figure 3 shows the graph of the membrane output in relative units $L/L(\gamma = 0, \Delta T = 0)$ against ΔT at different values of γ for the composition $x_1 = 0.3$. Curves 3 and 4 intersect the abscissa axis at the points where $x_1 = \gamma_1^* x_1'$. The break points of curves 1 and 2 correspond to $Q_2^* = 0$. The membrane output becomes zero on curves 1 and 2 at points where $Q_1^* = 0$ and $x_1 = \gamma_1^*$, respectively.

In summary, in our study we have shown that the separation effect and output of a membrane under nonisothermal conditions are determined by the process parameters and have also determined the limits of the separation effect of binary gas mixtures.

NOTATION

N, number of components of the mixture being separated; x_i, concentration of the i-th component in the high-pressure chamber; P_1, gas pressure in the HPC; T_1, gas temperature in the HPC; x_i', concentration of the i-th component in the low-pressure chamber; P_2, gas pressure in the LPC; T_2, gas temperature in the LPC; u_i, average (over the pore cross section) velocity of the i-th component of the mixture; a_i and c_i, coefficients that depend on the interaction of the i-th component of the mixture with the pore surface; V_i, mean thermal velocity of the i-th component; d, pore diameter; ρ_i, density of the i-th component of the mixture; T, gas temperature; λ_F, phonon mean free path in the material of the membrane; j_i, flux density of the i-th component penetrating through the longitudinal section of the porous membrane; ε, porosity coefficient of the membrane; ξ, pore sinuosity coefficient; $\bar{d}$, mean diameter of pores in the membrane; R, the universal gas constant; p_i is the partial pressure of the i-th component of the mixture; z is the coordinate; p_{1i}, p_{2i}, partial pressures of the i-th component of the mixture before and after the membrane, respectively, δ, membrane thickness; Q_i^*, permeability of the porous membrane for the i-th component of the mixture through the porous membrane under the conditions of Knudsen flow; m_i, molar mass of the i-th component.

LITERATURE CITED

1. V. D. Borman, S. Yu. Krylov, A. V. Prosyanov, and A. M. Kharitonov, Zh. Eksp. Teor. Fiz., 90, No. 1, 76 (1986).
2. V. D. Borman, S. Yu. Krylov, and A. M. Kharitonov, Pis'ma Zh. Tekh. Fiz., 11, No. 7, 430 (1985).
3. V. D. Borman, S. Yu. Krylov, and A. M. Kharitonov, Pis'ma Zh. Tekh. Fiz., 12, No. 12, 13 (1986).
4. S. Villani (ed.), Uranium Enrichment [Russian translation], Moscow (1983).
5. S.-T. Hwang and K. Kammermeyer, Membranes in Separation, Wiley, New York (1975).
6. V. D. Borisevich, V. Yu. Kozhevnikov, N. I. Laguntsov, and G. A. Sulaberidze, Teor. Osn. Khim. Tekhnol., 17, No. 1, 60 (1983).