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MEMBRANE SELECTIVE SEPARATION OF BINARY GAS MIXTURES

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A general approach to solving a conjugate problem of mass transfer in the separation of binary gas mixtures in selectively permeable membrane elements with allowance for the external convective and intramembrane diffusion resistances is suggested.

Introduction. In the last decade of the previous century and at the beginning of the new one, there has been a considerable upswing of interest in the apparatuses and devices that separate gas mixtures of various compositions on the basis of selectively permeable membranes [1–9]. This is ascribed to the fact that the traditionally used technologies (cryogenic, adsorption-based) have attained their limit from the viewpoint of their further optimization and adaptation to the increased requiremeents of industry. The use of membrane facilities allows one to considerably intensify the process of gas mixture separation. Thus, for example, the average cost of obtaining one liter of nitrogen from air by means of a gas-separating membrane module of the Klimbi company is 50% lower than that produced traditionally by a cryogenic technique. Among the advantages of the membrane method are the ecological purity of the process, reliable operation, compactness, explosion- and fire-safety, flexible characteristics of separation and their smooth regulation, independence of operation, and the mobility of the process — the possibility of continuous and periodic modes of operation [5]. Gas-separating facilities are finding application in various branches of science and technology: separation of a synthesis gas, production of nitrogen and oxygen directly from air, purification and creation of air-breathing mixtures, creation of a protective atmosphere in fire- and explosion-hazardous processes, storing of agricultural products and antiques, etc.

The mechanism underlying the membrane method of separation of gas mixtures is at the study stage. This is attributable to a multitude of factors that influence the process: a wide range of gas mixtures varying in their physical properties; diverse implementation of membrane separation (shape of the channel, flow velocity, excess pressure, initial concentration, etc.); membranes varying in the material and, as a consequence, in their physicochemical properties exerting their influence on permeability and selectivity.

In [1, 2], consideration is given to some laws that govern mass transfer in membrane elements on the assumption that injection (suction) of a gas mixture does not change the properties of the main flow, whereas the gas dynamics of the flow is independent of the separation process on a membrane and is determined by the relations that follow from Berman's solutions [6]. In [1, 7], the laws governing mass transfer in the head channel of the membrane element are considered on the basis of the analogy with the heat-transfer problem. The disadvantage of these works is that in the case of the membrane element of gas-separating module it is necessary to solve a more complex problem of conjugate mass transfer in the head channel and membrane, when the magnitude of the rate of penetration of a gas mixture $\overline{V}_{\overline{r}=R} = \overline{V}(\overline{x})$ is the unknown quantity and cannot be assigned a priori as a boundary condition.

Despite the intense development of membrane technology, many problems have remained inadequately studied. In particular, there is no uniformity of opinion on the best type of membrane and apparatuses for gas separation. There are no strict criteria and recommendations for selecting optimal dimensions of the membrane complex. There are no reliable mathematical models allowing one to predict the process of gas separation at the given characteristics of the membrane and mixture composition.

At the present time, asymmetrical polymer membranes have been created and are being actively used, which consist of a working layer of thickness 0.01–2 μm and a porous backing of the same polymer of thickness 20–150 μm

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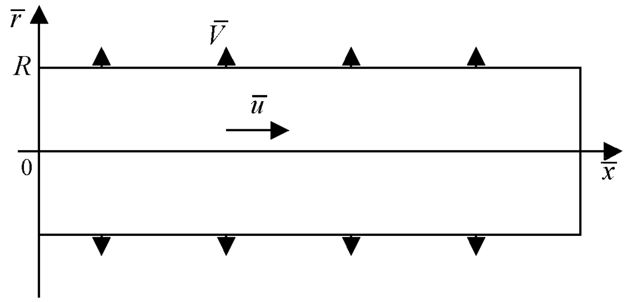

Fig. 1. Schematic of a flow-through membrane gas-separation module.

for separation of gas mixtures. To calculate modules incorporating these membranes one has to solve a conjugate problem of convective mass transfer in the head channel and of mass transfer through the membrane. Such a problem for a semipermeable membrane has been posed for the first time and solved in [10, 11]. In what follows, we consider mass transfer of a binary gas mixture in the membrane element with a selectively permeable membrane (i.e., with a membrane having a nonideal selectivity), since precisely this situation is realized in practice.

Analytical Theory of Membrane Gas Separation. The concern of the present investigation is the development of a mathematical model of baromembrane selective gas separation and the study, on its basis, of the operation of gas-separating membrane elements. Modeling will make it possible to determine the optimum length of the membrane module, pressure in the head channel, and rate of penetration, which ensure the maximum efficiency at the prescribed properties of the membrane and initial concentration of the gas being separated to obtain the prescribed purity of the separated gas.

The base unit of the membrane facility is the gas-separating module fabricated on the basis of plane-frame or hollow-fiber elements made from polymer membrane material. A binary gas mixture with a concentration of an easily penetrating component c_0 enters into the head channel of the membrane element (see Fig. 1). As a result of the different rates of penetration of the components during flow through the membrane, the composition of the mixture undergoes a change. In the head channel the fraction of the easily penetrating component is decreased as a result of passage through the drainage channel and the concentration of the almost impenetrable component is increased. The mixtures of gases from the head and drainage channels are delivered from the membrane element. The resistance of the drainage channel is not taken into account in this work.

We assume the gas mixture to be binary. The head channel is a plane slit or a hollow fiber. The flow in the head channel is two-dimensional and symmetrical relative to the channel axis, laminar, steady, and fully developed at the entrance to the channel. The gas mixture is incompressible, the process is isothermal, the coefficients of viscosity and diffusion are constant. The second viscosity and barodiffusion are neglected. For diffusion of gases in polymers with a low critical temperature the coefficients of permeability Λ are usually independent of gas concentration in the membrane and are considered constant. Then the equations of continuity, motion, and of convective diffusion in a dimensionless form are

$$\frac{\partial u}{\partial x} + r^{-\alpha} \frac{\partial (r^{\alpha} v)}{\partial r} = 0 , \tag{1}$$

$$\frac{\partial p}{\partial x} = \frac{1}{\mathrm{Re}\,\varepsilon} \left[r^{-\alpha} \frac{\partial}{\partial r} \left(r^{\alpha} \frac{\partial u}{\partial r} \right) \right], \quad \frac{\partial p}{\partial r} = 0 , \tag{2}$$

$$u \frac{\partial c}{\partial x} + v \frac{\partial c}{\partial r} = \frac{1}{\mathrm{Pe}_D\, \varepsilon} r^{-\alpha} \frac{\partial}{\partial r} \left(r^{\alpha} \frac{\partial c}{\partial r} \right), \tag{3}$$

at the boundary conditions:

at the entrance to the channel (at $x = 0$)

$$c = c_0\,, \quad p = p_0\,, \quad u = \frac{\alpha + 3}{2}\left(1 - r^2\right), \tag{4}$$

on the axis (in the plane) of symmetry (at $r = 0$)

$$\frac{\partial u}{\partial r} = 0\,, \quad v = 0\,, \quad \frac{\partial c}{\partial r} = 0\,, \tag{5}$$

on the membrane (at $r = 1$)

$$u = 0\,, \tag{6}$$

$$\left[(1 - c\,(x, r))\, v\,(x, r) + \frac{1}{\mathrm{Pe}_D\, \varepsilon} \frac{\partial c\,(x, r)}{\partial r}\right]\Bigg|_{r=1} = \Lambda_2 M_2\, (1 - c_{\mathrm{w}}\,(x))\, \frac{p\,(x)\, u_0}{\delta_{\mathrm{m}} \varepsilon}\,. \tag{7}$$

The rate of penetration of a gas mixture $V(x)$ with different coefficients of penetration of components through a selective membrane is taken to be linearly dependent on the pressure over the membrane and is determined from the equation

$$v\,(x, 1) = V\,(x) = \left(\Lambda_1 M_1 c_{\mathrm{w}}\,(x) + \Lambda_2 M_2\, (1 - c_{\mathrm{w}}\,(x))\right) \frac{p\,(x)\, u_0}{\delta_{\mathrm{m}} \varepsilon}\,. \tag{8}$$

The equations of continuity, motion, and convective diffusion (1)–(3) are interrelated, since the unknown rate of penetration of the gas mixture $V(x)$ depends on the concentration $c_{\mathrm{w}}(x)$ and pressure $p(x)$ on the channel wall. For solving the problem we assume that the rate $V(x)$ is a certain, as yet unknown, function of the longitudinal coordinate x, which allows one to solve the equations of motion and of convective diffusion independently.

In solving the equations of continuity and motion (1), (2), subject to boundary conditions (4)–(6), we find the distributions of the rates and pressure in the membrane channel [10]:

$$u\,(x, r) = \frac{(\alpha + 3)}{2}\left(1 - (\alpha + 1) \int_0^x V\,(x)\, dx\right)\left(1 - r^2\right), \tag{9}$$

$$v\,(x, r) = \frac{(\alpha + 1)\,(\alpha + 3)}{2}\, V\,(x) \left(\frac{r}{\alpha + 1} - \frac{r^3}{\alpha + 3}\right), \tag{10}$$

$$p\,(x) = p_0 - \frac{(\alpha + 1)\,(\alpha + 3)}{\mathrm{Re}\, \varepsilon} \int_0^x \left(1 - (\alpha + 1) \int_0^x V\,(x)\, dx\right) dx\,. \tag{11}$$

To analyze the equation of convective diffusion (3) a semi-integral method is proposed. The essence of the method is that the distribution of concentration in the diffusion layer is determined directly from the equation of convective diffusion in the region adjacent to the membrane. Using the continuity equation (1), we will write the equation of convective diffusion in a conservative form:

$$\frac{\partial\,(r^\alpha u\,(1 - c))}{\partial x} + \frac{\partial}{\partial r}\left[\frac{1}{\mathrm{Pe}_D} r^\alpha \frac{\partial c}{\partial r} + r^\alpha v\,(1 - c)\right] = 0\,. \tag{12}$$

We will drop the first term of the equation; this yields

$$\frac{\partial}{\partial r}\left[\frac{1}{\mathrm{Pe}_D} r^\alpha \frac{\partial c}{\partial r} + r^\alpha v\,(1 - c)\right] = 0\,. \tag{13}$$

Integration of Eq. (13) over the coordinate r, with allowance for boundary conditions (5), (6) and rate distribution (10), results in

$$c(x, r) = 1 - \left(1 - c_{\mathrm{w}}(x)\right)\exp\left(-\mathrm{Pe}_D \varepsilon V(x)\left(\frac{\alpha+5}{8} - \frac{\alpha+3}{4} r^2 + \frac{\alpha+1}{8} r^4\right)\right). \tag{14}$$

The distribution of concentrations (14) is exact near the membrane. The concentration profile over the entire section of the membrane channel can be found by using the integral equation of mass balance. For this purpose, we integrate Eq. (12) over the coordinate r from 0 to 1 with allowance for boundary conditions (7):

$$\frac{d}{dx}\int_0^1 r^\alpha u(x, r)\,(1 - c(x, r))\,dr = -\Lambda_2 M_2 (1 - c_{\mathrm{w}}(x))\frac{p(x)\,u_0}{\varepsilon\delta_{\mathrm{m}}}. \tag{15}$$

Estimation shows that for gas mixtures with a laminar mode of flow the zone of diffusional boundary layer occupies a small portion of the membrane-channel length and can be neglected [12]. For membrane separation of gases small values of $\mathrm{Pe}_D \varepsilon V(x)$ are typical, hence the exponent can be expanded into a series, and we can restrict ourselves to the first two terms of expansion, neglecting terms of the order $(\mathrm{Pe}_D \varepsilon V(x))^2$:

$$\exp\left(-\mathrm{Pe}_D \varepsilon V(x)\left(\frac{\alpha+5}{8} - \frac{\alpha+3}{4} r^2 + \frac{\alpha+1}{8} r^4\right)\right) =$$

$$= 1 - \mathrm{Pe}_D \varepsilon V(x)\left(\frac{\alpha+5}{8} - \frac{\alpha+3}{4} r^2 + \frac{\alpha+1}{8} r^4\right) + O\left((\mathrm{Pe}_D \varepsilon V(x))^2\right). \tag{16}$$

Using the distributions of rate (9) and concentration (14), the integral mass balance equation can be presented in the form

$$\frac{d}{dx}\int_0^1\left[r^\alpha \frac{(\alpha+3)}{2}\left(1 - (\alpha+1)\int_0^x V(x)\,dx\right)\left(1 - r^2\right)\left(1 - c_{\mathrm{w}}(x)\right)\times\right.$$

$$\left.\times\exp\left(-\mathrm{Pe}_D \varepsilon V(x)\left(\frac{\alpha+5}{8} - \frac{\alpha+3}{4} r^2 + \frac{\alpha+1}{8} r^4\right)\right)\right] dr = -\Lambda_2 M_2 (1 - c_{\mathrm{w}}(x))\frac{p(x)\,u_0}{\varepsilon\delta_{\mathrm{m}}}. \tag{17}$$

We will transform Eq. (17), subject to (16), as

$$\frac{d}{dx}\left((\alpha+1) - \int_0^x V(x)\,dx\right)\left(1 - c_{\mathrm{w}}(x)\right)\left(1 - \frac{(17+5\alpha)\,\mathrm{Pe}_D \varepsilon V(x)}{(5+\alpha)(7+\alpha)}\right) = -\Lambda_2 M_2 (1 - c_{\mathrm{w}}(x))\frac{p(x)\,u_0}{\varepsilon\delta_{\mathrm{m}}}. \tag{18}$$

Having determined from Eq. (8) the near-membrane concentration $c_{\mathrm{w}}(x)$ for the penetration rate $V(x)$ and substituting it into (18), we will obtain an integro-differential equation which makes it possible to calculate the most important characteristics of the membrane separation of binary gas mixtures, that is, the rate of penetration:

$$\frac{d}{dx}\left[\left((\alpha+1) - \int_0^x V(x)\,dx\right)\left(1 - \frac{V(x)}{p(x)}\frac{\delta_{\mathrm{m}}\varepsilon}{\Lambda_1 M_1 u_0}\right)\left(1 - \frac{(17+5\alpha)\,\mathrm{Pe}_D \varepsilon V(x)}{(5+\alpha)(7+\alpha)}\right)\right] =$$

$$= -\frac{\Lambda_2 M_2 u_0}{\delta_{\mathrm{m}}\varepsilon}\,p(x)\left(1 - \frac{V(x)}{p(x)}\frac{\delta_{\mathrm{m}}\varepsilon}{\Lambda_1 M_1 u_0}\right). \tag{19}$$

To find the dependence of the penetration rate on the longitudinal coordinate x, we use a number of simplifying assumption. Using the expression for the dependence of pressure on the longitudinal coordinate (11), we obtain

$$p(x) = p_0 - \frac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon} x + \frac{(\alpha+1)^2(\alpha+3)}{\mathrm{Re}\,\varepsilon} \int_0^x \left(\int_0^x V(z)\,dz \right) dx \,. \tag{20}$$

At the characteristic values of the membrane separation of gas mixtures ($u_0 \sim 10^0$–10^1, $\varepsilon \sim 10^{-4}$–10^{-3}, penetration rate $V(x) \sim 10^{-3}$–10^{-1}, and $\mathrm{Re} < 2000$), we estimate from above the pressure in a module of length L, having assumed that $V(x) = V$:

$$p(x) = p_0 - \frac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon} x + \frac{(\alpha+1)^2(\alpha+3)}{2\mathrm{Re}\,\varepsilon} x^2 V \,. \tag{21}$$

Since the third term is small in comparison with the remaining terms, it can be neglected within one element. In this case, Eq. (19) takes the form

$$\frac{d}{dx}\left[\left((\alpha+1) - \int_0^x V(x)\,dx\right)\left(1 - \frac{V(x)}{p_0 - \frac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon} x} \frac{\delta_{\mathrm{m}}\varepsilon}{\Lambda_1 M_1 u_0}\right)\left(1 - \frac{(17+5\alpha)\,\mathrm{Pe}_D \varepsilon V(x)}{(5+\alpha)(7+\alpha)}\right)\right] =$$

$$= -\frac{\Lambda_2 M_2 u_0}{\delta_{\mathrm{m}}\varepsilon}\left(p_0 - \frac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon} x - V(x) \frac{\delta_{\mathrm{m}}\varepsilon}{\Lambda_1 M_1 u_0}\right). \tag{22}$$

Thus, the integro-differential equation (22) is the most important relation for the rate of penetration $\overline{V}$ of a gas mixture through a membrane with account for the nonideal selectivity of the membrane, external diffusional convective and intramembrane diffusion resistances, the physical properties of a gas mixture (c, D, M_1, M_2, ν, ρ), the physicochemical properties of a membrane (Λ_1, Λ_2), the technological parameters of the process ($\overline{p}$, u_0), and the geometry and dimensions of the membrane element (R, L, δ_{m}). In the case of a semipermeable membrane ($\Lambda_2 = 0$), relation (22) agrees with the particular solution of [10].

CONCLUSIONS

1. A mathematical model that describes the process of separation of a binary gas mixture in a selective membrane element with account for convective external and intramembrane diffusion resistances has been developed.
2. A semi-integral method for investigating the process of membrane gas separation with nonideal selectivity of the membrane is suggested.
3. An integro-differential equation has been obtained for the most important characteristic of baromembrane separation — the rate of penetration depending on the properties of the gas mixture, technological parameters of the process, physicochemical properties of the membrane, and the geometry and dimensions of the membrane element.

NOTATION

c, concentration of an easily penetrating component; D, diffusion coefficient, m^2/sec; L, channel length, m; M, molar mass of a penetrating component, kg/mole; $\overline{p}$, pressure, Pa; $p = \overline{p}/(\rho u_0^2)$, dimensionless pressure; $\mathrm{Pe}_D = u_0 R/D$, diffusion Peclet number; R, radius (halfwidth) of a channel, m; $\overline{r}$, radial coordinate, m; $r = \overline{r}/R$, dimensionless radial coordinate; $\mathrm{Re} = u_0 R/\nu$, Reynolds number; $\overline{u}$, longitudinal projection of rate, m/sec; $u = \overline{u}/u_0$, dimensionless longitudinal projection of rate; u_0, mean flow rate at the inlet to the channel, m/sec; υ = radial projection of rate, m/sec; $\upsilon = \overline{\upsilon}L/(u_0 R)$, dimensionless radial projection of rate; $\overline{V}$, penetration rate, m/sec; $V = \overline{V}L/(u_0 R)$, dimensionless rate of penetration; $\overline{x}$, longitudinal coordinate, m; $x = \overline{x}/L$, dimensionless longitudinal coordinate; α, characteristic of the channel geometry ($\alpha = 0$ corresponds to a plane-frame channel, $\alpha = 1$ — to a hollow-fiber one); δ_{m}, effective thickness of a membrane, m; $\varepsilon = R/L$, ratio between two characteristic dimensions of the channel; Λ, penetration coefficient of the membrane, mole·m/(N·sec); ν, kinematic viscosity, m^2/sec; ρ, density, kg/m^3. Subscripts and superscripts: 0, value at the entrance into a channel; 1, and 2, easily and poorly penetrating components; m, membrane; w, value at the channel wall; bar from above, dimensional quantity.

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