PERMEATION RATE IN SELECTIVE MEMBRANE GAS SEPARATION

V. I. Baikov and N. V. Primak   UDC 66.071.6.081.6

The procedure of calculation of the permeation rate in membrane selective separation of binary gas mixtures with allowance for the convective external and intramembrane diffusion resistances has been proposed. The calculated concentration distributions in the membrane pressure channel have been compared to the literature experimental data; their satisfactory agreement has been shown. The ordinary nonlinear differential equation of first order for the permeation rate as a function of the physical properties of a binary gas mixture and the parameters of a membrane element has been solved.

Introduction. Traditional energy resources, such as petroleum, coal, and gas, are not renewable; therefore, it is important to find alternative fuel sources. One environmentally balanced method involves the utilization of waste with the aim of obtaining high-grade fuel gases (methane and hydrogen). In the chemical industry, in producing ammonia, methanol, and petroleum-refining products, one does not utilize hydrogen completely; most of it is lost, being part of waste gases or is used as a low-calorie fuel. In this connection, it seems very promising to use the membrane method of obtaining of hydrogen from gas mixtures [1–3]. This is due to the high selectivity and permeability of polymeric and metal membranes to hydrogen and to the low cost of the membrane method of obtaining of hydrogen. However, not only must one solve a number of technological and instrumental problems for the membrane processes of gas separation to be commercialized, but one must also create calculation methods for these processes.

There are no efficient methods of calculation of the processes of convective mass exchange of a binary gas mixture in a selectively permeable membrane element at present. The complex pattern of flow gas separation on the membrane with nonideal selectivity made it impossible to propose a mathematical model fairly well describing the process of separation of gas mixtures; therefore, a number of substantial assumptions were made. Flows with a constant permeation rate have been considered in most works, and the condition of semipermeability of the membranes has been used [4–8]. In the separation of gas mixtures, one is usually dealing with selectively permeable membranes; therefore, all components of the mixture but with different velocities penetrate from the pressure channel through the walls of the separating element. Since the driving force of component transfer is determined by the difference of the chemical potentials in pressure and drain channels, the permeation rate of each component varies with membrane-element length and is dependent on the thermodynamic and hydrodynamic parameters of the process. The dimensionless rate $V = VL/(u_0 R)$ represents the ratio of the rates of flow of the gas through the membrane and of the mixture through the channel cross section. The rate of permeation of the gas mixture through the selective membrane $V(x)$ with different permeability coefficients for the components is taken to be linearly dependent on the pressure above the membrane and is determined from the equation of permeation through the membrane

$$V(x) = (\Lambda_1 M_1 c_{\text{w}}(x) + \Lambda_2 M_2 (1 - c_{\text{w}}(x))) \frac{p(x) u_0}{\delta_{\text{m}} \varepsilon} .$$

A correct description of the conjugate problem of convective and intramembrane mass transfer in the selective membrane element (Fig. 1) of a binary gas mixture has been proposed in [9], where the main result is derivation of the integro-differential equation

---
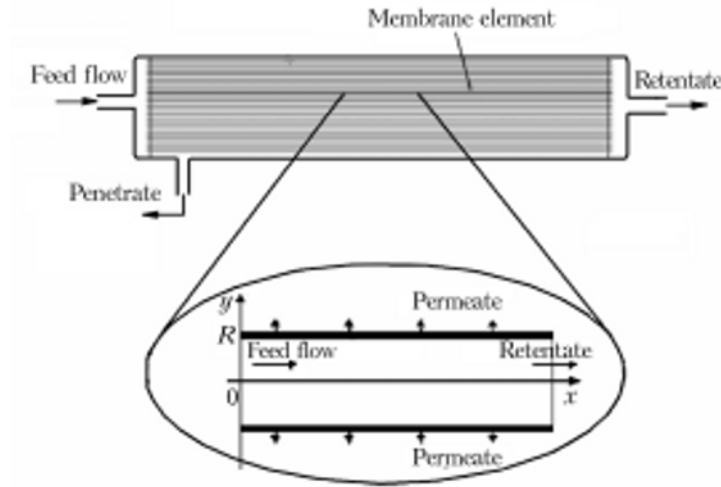
Fig. 1. Diagram of a flow membrane gas-separating module.

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

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

for the permeation rate $V(x)$ of the selective membrane with allowance for convective and intramembrane diffusion resistances.

Mathematical Model. The present work seeks to develop the procedure of solution of Eq. (1), that will enable us to analyze the process of separation of the mixture in the gas-separating element with selectively permeable membranes and to evaluate the prospects for searching polymeric materials suitable for manufacture of selectively permeable membrane elements to isolate hydrogen from synthesis gas.

Let us transform the integro-differential equation (1) to a differential one. For this purpose we introduce the notation

$$\int_0^x V(x)\,dx=\theta(x),\quad \theta'(x)=V(x),\quad A_1=\frac{\Lambda_1 M_1 u_0}{\delta_\mathrm{m}\varepsilon},\quad A_2=\frac{\Lambda_2 M_2 u_0}{\delta_\mathrm{m}\varepsilon}$$

and pass from the variable $V(x)$ to a new variable $\theta(x)$

$$\frac{d}{dx}\left[\left(\frac{1}{\alpha+1}-\theta(x)\right)\left(1-\frac{\theta'(x)}{p_0-\dfrac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon}x}\frac{1}{A_1}\right)\left(1-\frac{(17+5\alpha)\,(\mathrm{Pe}_D\varepsilon\theta'(x))}{(5+\alpha)(7+\alpha)}\right)\right]$$

$$=-A_2\left(p_0-\frac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon}x-\theta'(x)\frac{1}{A_1}\right). \tag{2}$$

We integrate relation (2) with respect to the coordinate x with allowance for the boundary conditions

$$\theta(0)=0,\quad \theta'(0)=V(0)=p_0 A_1\left[c_0\left(1-\frac{A_2}{A_1}\right)+\frac{A_2}{A_1}\right]. \tag{3}$$

Then we obtain the quadratic equation for the derivative $\theta'(x)$

$$a(x)(\theta'(x))^2 + b(x)\theta'(x) + d(x) + \frac{e(x)}{(\alpha+1)^{-1} - \theta(x)} = 0, \tag{4}$$

where

$$a(x) = \frac{(17 + 5\alpha)\,\mathrm{Pe}_D\varepsilon}{\left(p_0 - \dfrac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon}x\right)A_1\,(5+\alpha)(7+\alpha)}\,; \quad b(x) = -\frac{(17+5\alpha)\,\mathrm{Pe}_D\varepsilon}{(5+\alpha)(7+\alpha)} - \frac{1}{p_0 - \dfrac{(\alpha+1)(\alpha+3)}{\mathrm{Re}\,\varepsilon}x}\frac{1}{A_1}\,;$$

$$d(x) = \frac{A_2}{A_1} + 1\,; \quad e(x) = -\frac{1}{(\alpha+1)}\left[\left(1 + \left(\frac{A_2}{A_1} - 1\right)\frac{(17+5\alpha)\,\mathrm{Pe}_D\varepsilon\,p_0\left(c_0\left(1 - \dfrac{A_2}{A_1}\right) + \dfrac{A_2}{A_1}\right)A_1}{(5+\alpha)(7+\alpha)}\right)(1 - c_0) + c_0\frac{A_2}{A_1}\right]$$

$$+ A_2\left(p_0 x - \frac{(\alpha+1)(\alpha+3)}{2\,\mathrm{Re}\,\varepsilon}x^2\right).$$

In solving the quadratic equation (4), we select a minus sign to satisfy boundary condition (3) for $x = 0$

$$\theta'(x) = \frac{-b(x) - \sqrt{b^2(x) - 4a(x)\left(d(x) + \dfrac{e(x)}{(\alpha+1)^{-1} - \theta(x)}\right)}}{2a(x)}. \tag{5}$$

The ordinary nonlinear differential equation of first order (5) is solved by the Runge–Kutta method of fourth order. The resulting solution is substituted into the expression for the near-membrane concentration

$$c_w(x) = \frac{\dfrac{V(x)}{p(x)} - A_2}{A_1 - A_2}. \tag{6}$$

Numerical Experiment and Comparison to Experimental Data. To check the developed method of calculation of the gas separation we compare numerical and experimental data. Experiments on separation of helium from nitrogen from the binary mixture of these gases are presented in [5, 10]. The gas-separating module manufactured from plane-frame elements of "Vikor" porous membrane sheet glass, where nitrogen is a less penetrating gas, was the basic unit of the setup. The membrane area in the module was 0.0117 m^2, the pressure in the pressure channel was $\bar{p}_0 = 0.254$ MPa, the ratio of the permeabilities of helium and nitrogen was $\beta = 2.35$, and the mixture flow rate was $1.8\cdot10^{-6}$ m^3/sec. The regime of flow of the gas mixture in the channel was laminar. Since the interdiffusion coefficient and the viscosity of the gas mixture η are not presented in the cited works, they were borrowed from [11] for the interdiffusion coefficient $D_{T=298K}\bar{p} = 6.96$ m^2·Pa/sec, and from [12] for calculation of the viscosity of the gas mixture η:

$$\eta = \frac{\eta_1}{1 + \dfrac{1-c}{c}\dfrac{M_1}{M_2}\left(1 + \sqrt{\dfrac{\eta_1}{\eta_2}}\sqrt[4]{\dfrac{M_2}{M_1}}\right)^2 \Big/ \sqrt{8 + \dfrac{8M_1}{M_2}}} + \frac{\eta_2}{1 + \dfrac{c}{1-c}\dfrac{M_2}{M_1}\left(1 + \sqrt{\dfrac{\eta_2}{\eta_1}}\sqrt[4]{\dfrac{M_1}{M_2}}\right)^2 \Big/ \sqrt{8 + \dfrac{8M_2}{M_1}}},$$

where $\eta_1 = \eta_{\mathrm{He}|T=300K} = 1.975\cdot10^{-5}$ Pa·sec, $\eta_2 = \eta_{\mathrm{N}_2|T=300K} = 1.790\cdot10^{-5}$ Pa·sec, $M_1 = 4.0026$ kg/mole, $M_2 = 28.0134$ kg/mole, and $\nu = \eta/\rho = 0.97\cdot10^{-5}$ m^2/sec.
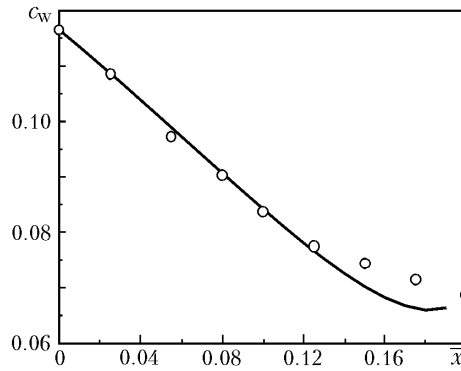
Fig. 2. Profiles of the near-membrane helium concentration in the pressure channel: points, experimental data; curve, calculation from the model proposed.

TABLE 1. Coefficient of Hydrogen and Carbon-Oxide Permeability (Λ) of Polymeric Membranes

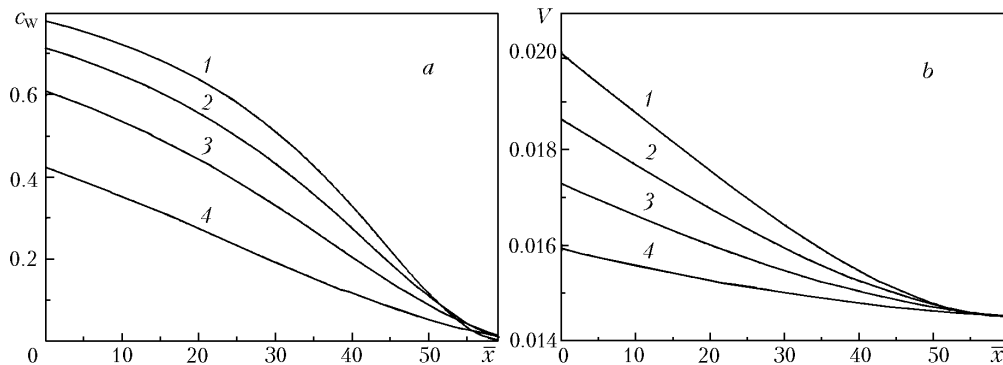| Polymer/Type of membrane	Selective-layer thickness, μm	$\Lambda \cdot 10^{15}$, mole·m/(m²·sec·Pa)	
		H_2	CO
"Gasep" cellulose acetate/A	0.1	11.0	0.27
"Dupont" cellulose acetate/A	9	89.4	0.73
"Ube Kosan" polyimide/B	0.2	1.11	0.009
"Dupont" polyimide/B	0.2	6.7	0.09

Note. A, plane membrane; B, hollow fibers.

Fig. 3. Concentration of hydrogen on the membrane surface (a) and permeation rate (b) vs. longitudinal coordinate for different concentrations of hydrogen in the starting mixture for the plane-frame ($\alpha = 0$) element with a membrane of "Gasep" cellulose acetate: 1) $c_0 = 0.20$, 2) 0.15, 3) 0.10, and 4) 0.05. c_w, wt. fraction.

A comparison of experimental data on the influence of the convective and intramembrane diffusion resistances on the helium-concentration distribution in the channel in the separation of the He–N$_2$ mixture on the glass membrane with the results of calculations from formula (6) is given in Fig. 2. A satisfactory agreement of the calculation results and experimental data is observed in the first half of the membrane channel, and a certain disagreement is observed in the second half of the channel. The reason is that no resistance to the mass transfer of the drain channel is allowed for in the model proposed, and the drain-channel pressure was 0.1 MPa in the experiment, which, probably, was responsible for the disagreement of the experimental and theoretical results.

In practice, in the separation of gas mixtures, one uses different gas-separating flow diagrams, including hollow-fiber and plane-frame modules based on membranes which are different in separating characteristics (Table 1).
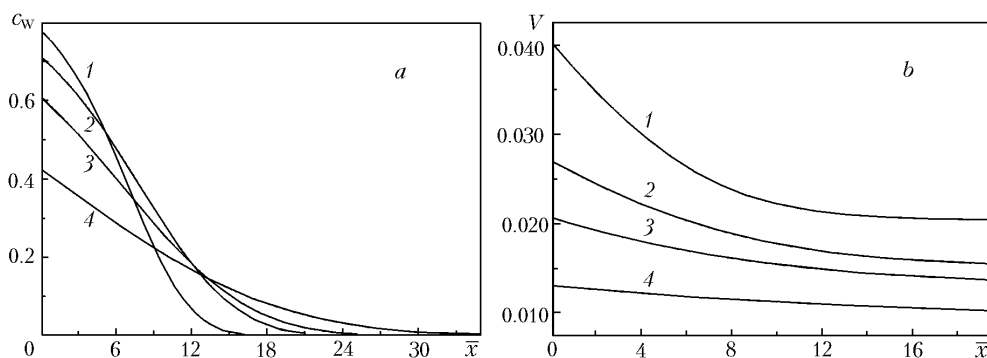
Fig. 4. Concentration of hydrogen on the membrane surface (a) and permeation rate (b) vs. longitudinal coordinate for different concentrations of hydrogen in the starting mixture for the hollow-fiber ($\alpha = 1$) element with a membrane of "Dupont" polyimide. Notation 1–4 is the same as that in Fig. 3.

TABLE 2. Comparison of Plane-Frame and Hollow-Fiber Elements

Polymer	Type of element	Output of the element, kg/sec	Density of the packing, m²/m³	Output of the module, kg/sec
"Gasep" cellulose acetate	$\alpha = 0$	$1.15 \cdot 10^{-4} s c_0$	1000	0.017 $s c_0$
"Dupont" polyimide	$\alpha = 1$	$2 \cdot 10^{-7} c_0$	20 000	0.45 c_0

The mathematical model proposed and the method of its solution enable us to analyze the permeation rate, the concentrations in the channel, and the output of the element for different parameters of the system. We have considered, as the gas mixture under study, synthesis gas consisting of CO and H_2 which are obtained in processing of natural gas, petroleum products, and wood and by gasification of coals. For calculations, we used the following values of the parameters: $M_1 = 2 \cdot 10^{-3}$ kg/mole, $M_2 = 28 \cdot 10^{-3}$ kg/mole, and $u_0 = 1$ m/sec; $R = 10^{-3}$ m and $\bar{p} = 5$ atm for $\alpha = 0$ and $R = 10^{-4}$ m and $\bar{p}_0 = 50$ atm for $\alpha = 1$.

Figures 3 and 4 plot the concentration of hydrogen on the membrane surface and the permeation rate as functions of the length and geometry of the selective membrane element. The plots represent monotonically dropping curves. The efficiency of the isolation of hydrogen is substantially influenced by the content of carbon oxide in the mixture and the relation between the permeability coefficients of the gases. Reduction in the channel length for a prescribed membrane area is necessary for decreasing the carbon-oxide loss.

The membrane module must ensure the maximum desired-component output for prescribed technological conditions. The output q and the surface area of the membrane in the module F are related by the kinetic relation

$$q_1 = \int_0^E \rho \bar{V}_1 (x) \, dF . \tag{7}$$

Modules made of hollow fibers are of greater interest than membrane plane-frame modules, since using them one can create a separating surface of to 20,000 m² in 1 m³ of a hollow-fiber packing for separation of gas mixtures. The output of the plane-frame element is larger than that of the hollow-fiber one (Table 2), but the density of the packing of plane-frame element attains just 1000 m²/m³. Therefore, the use of hollow fibers as membrane elements ensures the largest specific membrane surface per module-volume unit, which contributes to the creation of compact and high-yield apparatuses.

CONCLUSIONS

1. The procedure of numerical modeling of the processes of selective membrane gas separation of a binary mixture has been developed. The model has been verified.

2. The permeation rate in the process of separation of hydrogen from carbon oxide in synthesis gas has been investigated.

3. The output of membrane elements with different selectively permeable polymeric membranes as a function of the initial concentration of hydrogen in synthesis gas has been calculated.

NOTATION

c, concentration of the easily penetrating component, wt. fraction; D, diffusion coefficient, m^2/sec; F, membrane area, m^2; L, channel length, m; M, molar mass of the penetrating component, $kg/mole$; $\bar{p}$, pressure, Pa; $p = \bar{p}/(\rho u_0^2)$, dimensionless pressure; $Pe_D = u_0 R/D$, diffusion Peclet number; q, output, kg/sec; R, channel radius (half-width), m; $Re = u_0 R/\nu$, Reynolds number; s, channel width, m; $\bar{u}$, longitudinal projection of velocity, m/sec; $u = \bar{u}/u_0$, dimensionless longitudinal projection of velocity; u_0, mean-flow-rate velocity at entry into the channel, m/sec; $\bar{V}$, permeation rate, m/sec; $V = \bar{V}L/(u_0 R)$, dimensionless permeation rate; $\bar{x}$, longitudinal coordinate, m; $x = \bar{x}/L$, dimensionless longitudinal coordinate; α, characteristic of the channel geometry ($\alpha = 0$ corresponds to the plane-frame channel, $\alpha = 1$ corresponds to the hollow-fiber channel); $\beta = \Lambda_1 M_1/(\Lambda_2 M_2)$, selectivity of the membrane; η, dynamic viscosity, $Pa \cdot sec$; δ_m, effective membrane thickness, m; $\varepsilon = R/L$, ratio of the characteristic dimensions of the channel; Λ, permeability coefficient of the membrane, $mole \cdot m/(N \cdot sec)$; ν, kinematic viscosity, m^2/sec; ρ, density, kg/m^3. Subscripts: 0, value at entry into the channel; 1, easily penetrating component; 2, nonpenetrating component; m, membrane; w, value on the channel wall; $\bar{}$, dimensional quantity; $'$, derivative of the function.

REFERENCES

1. N. A. Platé, Membrane technologies — a vanguard trend in the development of the science and technology of the 21st century, *Krit. Tekhnol. Membrany*, No. 1, 4–13 (1999).
2. U. Balachandran, T. H. Lee, L. Chen, S. J. Song, J. J. Picciolo, and S. E. Dorris, Hydrogen separation by dense cermet membranes, *Fuel*, **85**, 150–155 (2006).
3. M. Mulder, *Basic Principles of Membrane Technology* [Russian translation], Mir, Moscow (1999).
4. Yu. I. Dytnerskii, V. P. Brykov, and G. G. Kagramanov, *Membrane Separation of Gases* [in Russian], Khimiya, Moscow (1991).
5. S.-T. Hwang and K. Kammermayer, *Membrane Separation Processes* [Russian translation], Khimiya, Moscow (1981).
6. L. L. Murav'ev and L. A. Murav'ev, A model for calculation and optimization of hydrogen-permeable capillaries of membrane apparatuses, *Teor. Osnovy Khim. Tekhnol.*, **36**, No. 2, 176–180 (2002).
7. Hiromitsu Takaba and Shin-ichi Nakao, Computational fluid dynamics study on concentration polarization in H_2/CO separation membranes, *J. Membr. Sci.*, **249**, 83–88 (2005).
8. J. Zhang, D. Liu, M. He, H. Xu, and W. Li, Experimental and simulation studies on concentration polarization in H_2 enrichment by highly permeable and selective Pd membranes, *J. Membr. Sci.*, **274**, 83–91 (2006).
9. V. I. Baikov and N. V. Primak, Membrane selective separation of binary gas mixtures, *Inzh.-Fiz. Zh.*, **80**, No. 2, 161–165 (2007).
10. Yu. I. Kiselev, V. G. Karachevtsev, and V. N. Vetokhin, Modeling of a membrane gas-separation process with allowance for diffusional mixing in the element, *Teor. Osn. Khim. Tekhnol.*, **19**, Ni. 2, 177–183 (1985).
11. R. C. Reid, J. Prausnits, and T. K. Sherwood, *The Properties of Gases and Liquids* [Russian translation], Khimiya, Leningrad (1971).
12. I. F. Golubev and N. E. Gnezdilov, *The Viscosity of Gaseous Mixtures* [in Russian], Izd. Standartov, Moscow (1971).