fer parameters of the heat pipe with cellular material deteriorate appreciably (as is true of all classical heat pipes).

The advantages of a heat pipe with cellular material lie in the construction of plnar heat pipes, requirng rather a rigid capillary structure to achieve rigidity of the heat pipe structure. The evidence for this is the experimental data of heat pipes numbers 5, 6, and 7.

Thus, by using cellular materials as capillary structures, easily welded to the heat pipe body, and possessing enhanced strength properties with a porosity of more than 80%, one can build high-efficiency heat pipe structures which will fill the gap, to a certain extent, existing in practice in the manufacture and use of heat pipe panels.

NOTATION

P, porosity; $\overline{d}_h$, mean pore diameter; d, external diameter of the heat pipe body; a, width of the heat pipe; L, L_e, L_c, length of the heat pipe, and of the evaporation and condensation zones; δ, δ_b, δ_{cs}, thickness of the heat pipe, the body, and the capillary structure; K, permeability; σ_p, σ_{cm}, temporal resistance of the porous and compacted material; α, heat transfer coefficient; q, heat flux density; λ_p, λ_m, thermal conductivity of the porous and compacted material; φ, slope angle of the heat pipe to the horizontal; Q_{max}, maximum heat flux; $t_{\text{wall max}}^{\text{evap}}$, maximum wall temperature of the heat pipe body in the evaporation zone; R_{heat}, thermal resistance of the heat pipe; G, mass flow rate.

LITERATURE CITED

1. A. A. Popova, Instruments and Equipment of Electronic Apparatus, A Review, Moscow (1987).
2. S. V. Belov (ed.), Porous Permeable Materials: Handbook, Moscow (1987).
3. M. G. Semena, A. N. Gershuni, and V. K. Zaripov, Heat Pipes with Metal-Fiber Capillary Structures, Kiev (1984).
4. L. L. Vasil'ev, S. V. Konev, P. Shtul'ts, and L. Khorvat, Inzh. Fiz. Zh., Vol. 42, No. 6, 893-898 (1982).

FLOW OF PURE GASES IN POLYETHYLENE TEREPHTHALATE NUCLEAR ULTRAFILTRATION MEMBRANES

V. V. Ovchinnikov, V. D. Seleznev,
and V. I. Kuznetsov

UDC 621.039.341.22

Measurements have been made on the surface flow of hydrogen, nitrogen, krypton, and xenon in polyethylene terephthalate membranes having pore sizes less than 15 nm. The gas-selective behavior is considered and surface molecular migration coefficients are estimated.

Measurements have been made on the flow of pure gases in nuclear polyethylene terephthalate PETP membranes particularly because new types of membrane have recently been made that show high selectivity [1, 2]. Gas compnents can be separated because of differences in the diffusion and dissolution constants (Henry constants). The decisive features are the structure and the pore shape and size.

Pores are usually etched in polymer films to produce highly productive membranes. Porous semipermeable membranes [3] and nuclear ones [4, 5] are made in that way. A porous semipermeable membrane may be made by treating an amorphous-crystalline PETP film with crystallizing solvent solutions [6, 7] to raise the throughput by 2-3 orders of magnitude. However, when the pores become much larger than the gas molecules, the selectivity is largely lost, particularly if there is a large spread in pore sizes.

Joint Nuclear Research Institute, Dubna. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 1, pp. 73-77, January, 1990. Original article submitted August 10, 1987.

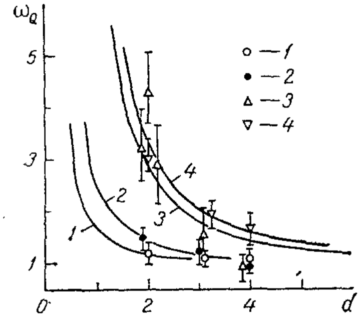

Fig. 1

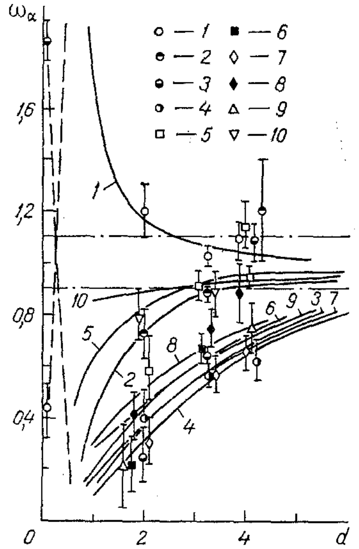

Fig. 2

Fig. 1. Dimensionless volume flow rate as a function of gas-dynamic pore diameter for: 1) H_2; 2) N_2; 3) Kr; 4) Xe, d, nm.

Fig. 2. Reduced ideal binary gas separation coefficient as a function of gas-dynamic pore diameter for: 1) He – He; 2) He – N_2; 3) He – Kr; 4) He – Xe; 5) H_2 – N_2; 6) H_2 – Kr; 7) H_2 – Xe; 8) N_2 – Kr; 9) N_2 – Xe; 10) Kr – Xe; dashed lines transition from straight cylindrical pores to semipermeable membranes; dot-dash line maximum random error of experiment.

Nuclear PETP membranes differ from other porous materials in that the pores have a regular cylindrical shape and less than 15% size spread. One can also more readily provide the optimum relation between the throughput and selectivity. Polycarbonate and PETP films have been the most widely used in nuclear membranes, which are made correspondingly by means of fission fragments in reactors [5] and heavy-ion irradiation in accelerators [4] followed by chemical treatment. The polymers (mainly PETP) are irradiated with heavy ions to produce nuclear membranes with more uniform pore geometry [4].

The published data on drying nuclear PETP membranes relate to ones with pore diameters over 15 nm [4, 8]. That restriction is [9] due to capillary contraction affecting the membrane during drying, which leads to an irreversible loss of porosity for pore sizes less than about 15 nm. However, that difficulty can be overcome by freeze-drying [10, 11], so it is possible to attain pore sizes comparable with the size of the etched regions for the heavy-ion track cores (about 2 nm [12]).

No measurements have been made on gas flow in that pore size range for nuclear PETP membranes, apart from our recent estimate for surface diffusion [13].

We have examined the flow of pure gases in these membranes for pore sizes of 2-15 nm.

When a gas at a pressure of 0.1 MPa flows into vacuum through a membrane with pores of those sizes, the bulk Knudsen flow rate is [13] as follows on the basis of equilibrium between the gas and adsorbed phases:

$$Q = \pi N d \left\{ K \frac{d}{2} + \frac{2 D_a \tau_a}{l} \right\} \frac{v_t}{8} \frac{\Delta P}{P} . \tag{1}$$

The first term here describes the Knudsen diffusion in the gas flow and the second the motion over the surface of the channels by adsorbed molecules (surface flow).

We rewrite (1) on the basis that $\ell/d > 10^3$ and $K = 4/3(d/\ell)$ in the form of the dimensionless volume flow rate of the gas ω_Q relative to the Knudsen diffusion:

$$\omega_Q = 1 + \frac{3D_a\tau_a}{d^2}. \tag{2}$$

The experiments were performed with membranes made in a standard way [4] from 10 μm PETP film. At the chemical treatment stage, the pore diameter was determined by conductometry [14]. The pore diameters in the dry membranes were monitored from the helium permeabilities [15, 16].

We examined the permeabilities for pure gases: helium, hydrogen, nitrogen, krypton, and xenon (purity not less than 99.99%) at room temperature. We determined ω_Q from the ratio to the helium flow rate, as helium does not [13, 17] give rise to an appreciable surface flow.

Figure 1 shows the measured ω_Q with corresponding standard deviations as functions of the gas-dynamic pore diameter d in the range where there is appreciable surface diffusion. Krypton and xenon give surface flows that exceed by about a factor three the diffusion in the gas for $d < 5$ nm, whereas nitrogen and hydrogen give such only for $d < 3$ nm.

The local-adsorption model is the most characteristic of these conditions [18]. One can write (2) as follows from the definition of the surface diffusion coefficient:

$$\omega_Q = 1 + 3\left(\frac{\delta}{d}\right)^2 \frac{\tau_a}{\tau}. \tag{3}$$

Frenkel's equation gives:

$$\tau = \tau_0 \exp\left(\frac{\varepsilon}{RT}\right), \tag{4}$$

and then (3) gives

$$\omega_Q = 1 + 3\left(\frac{\delta}{d}\right)^2 \exp\left(\frac{\varepsilon - E}{RT}\right). \tag{5}$$

In [13], δ was taken as 1 nm (the size of the unit cell in the PETP crystal), which makes the exponent in (5) negative for hdyrogen, i.e., not corresponding to the physical meaning of adsorption. It would appear better to take δ as equal to the length of the carbon chains in the PETP molecule, i.e., about 0.15 nm [19]. Then this was used with (5) for each gas to estimate $\varepsilon - E$. For H_2, N_2, Kr, Xe, the values were correspondingly 1.3; 1.8; 2.7 and 2.8 kcal/mole. The large errors in $\varepsilon - E$ are due to the considerable spreads in the ω_Q data, which are themselves due to plastic strain in the membrane loaded during the measurements. Fitted curves were constructed from (5) for each gas in Fig. 1.

As the molecular diffusion in the pores is independent, one can define relations between the pure-gas fluxes. In the capillary model, one uses the ideal separation coefficient α for a binary mixture, which is the ratio of the permeabilities for the gases:

$$\alpha = \frac{\Pi_1}{\Pi_2}, \quad \Pi_i = \frac{J_i}{S\,\dfrac{dP_i}{dx}}. \tag{6}$$

From (1), the flux J_i and thus the permeability Π_i may be written as

$$J_i = J_i^g + J_i^a, \quad \Pi_i = \Pi_i^g + \Pi_i^a. \tag{7}$$

By analogy with (2), (6) can be put in dimensionless form (relative to $\left[\frac{M_2}{M_1}\right]^{0,5}$)

$$\omega_\alpha = \frac{\omega_{Q1}}{\omega_{Q2}}. \tag{8}$$

Figure 2 shows the ω_α and corresponding (8) fitted curves as functions of gas-dynamic pore diameter for ten gas pairs. The surface flow reduces the ideal separation coefficient for virtually all pairs, but with helium-hydrogen and a pore diameter of about 2 nm, the ideal separation coefficient attains about 1.7, which corresponds to the lighter component (hydrogen) having the higher adsorption heat [20]. A similar result (ideal coefficient about 2) has recently been obtained for mica nuclear membranes with pore sizes below 5 nm [21].

The general fall in ω_α should be replaced by a step increase for semipermeable membranes, and for continous PETP, ω_α for He – N_2 ranges from about 60 to 125 [22] because of the completely different migration mechanism. The permeability involving unetched (latent) tracks in PETP formed by Xe ions does not involve a surface flow component. Figure 2 shows measurements for helium-hydrogen and helium-krypton pairs, which demonstrate the differences in diffusion mechanism for latent and tracks and straight cylindrical pores.

This type of surface flow (Fig. 1) indicates the migration for diatomic molecules for which $\varepsilon - E$ is small. The spatial configurations of the hydrogen and nitrogen molecules increase E relative to those barriers for the monatomic krypton and xenon. However, the adsorption always results in an additional diffusion or hydrodynamic transport mechanism for the heavy component. When the pore size is reduced to a few times the atomic dimensions, the entire pore space may be filled by the condensed heavy component, which penetrates preferentially. When the pore diameter is less than the molecular size for the heavy gas, the transport mechanism is by activated diffusion. In that case, helium and hydrogen atoms, which are small, may more readily diffuse into the polymer, e.g., for various organic gases for which ε is fairly large, polycarbonate nuclear membranes show such filling for $d \approx 40$ nm [23].

These measurements show that these membranes can be used to separate helium and hydrogen for pores of size less than 3 nm. There are prospects for separating isotopes [24, 25] and azeotropic gas mixtures [26].

NOTATION

Q, volume Knudsen gas flow; N, number of pores in nuclear membrane; d, pore diameter; D_a, surface diffusion coefficient; τ_a, mean time spent by a molecule in the adsorbed state; ℓ, membrane thickness; v_t, mean molecular thermal velocity; ΔP and P, pressure difference and mean pressure for gas in membrane; K, Clausing coefficient; δ, distance between adjacent molecular-adsorption areas; τ, mean time for an adsorbed molecule to jump from one equilibrium state to another; τ_0, difference in adsorbed-molecule vibrations perpendicular to surface; ε, adsorption heat; R, universal gas constant; T, absolute temperature; E, surface diffusion barrier; Π_i and J_i, permeability and flux for component i in membrane; P_i, pressure of component i; S, membrane area; J_i^g and Π_i^g, flux and permeability for component i in gas; J_i^a and Π_i^a, flux and permeability for component i in adsorbed state; M_1 and M_2, molecular weights of components 1 and 2.

LITERATURE CITED

1. M. G. Leibovskii, Modern Equipment for Membrane Methods of Separating Mixtures [in Russian], Moscow (1972).
2. "Advances in membranes for gas separation," Processing, 29, No. 1 (1983).
3. N. I. Nikolaev, Diffusion in Membranes [in Russian], Moscow (1980).
4. G. N. Flerov, Vestnik AN SSSR, No. 4, 35-48 (1984).
5. Nucleopore Filtration Products for the Laboratory. Catalog Lab. 50, Pleasanton, Calif. (1980).
6. E. P. Ageev, A. N. Neverov, N. L. Strusovskaya, and N. N. Savel'eva, Vestnik MGU, Khimiya, 23, No. 2, 75-87 (1982).
7. M. A. Krykin, V. V. Komakin, O. N. Tigina, et al., Zh. Fiz. Khim., 60, No. 4, 878-880 (1986).
8. P. Yu. Apel', V. I. Kuznetsov, N. I. Zhitaryuk, and O. L. Orelovich, Kolloidn. Zh., 47, No. 1, 3-8 (1985).
9. P. Yu. Apel', V. I. Kuznetsov, and V. V. Ovchinnikov, Capillary Contraction for Pores in Polymer Nuclear Membranes [in Russian], Dubna (1985). Preprint 18-85-376, Ob'edinennyi Institut Yadernykh Issledovanii.
10. V. P. Dubyaga, L. P. Perepechkin, and E. E. Katalevskii, Polymer Membranes [in Russian], Moscow (1981).
11. M. S. Ostrikov, N. D. Vishkevich, and O. D. Svirskaya, Kolloidn. Zh., 23, No. 1, 122-124 (1961).
12. P. Yu. Apel', A. Yu. Didyk, L. I. Kravets, et al., Processes in Radiation Chemistry and Track Structure in Polyethylene Terephthalate Bombarded by Heavy Ions [in Russian], Preprint R12-84-773, OIYaI, Dubna (1984).
13. V. V. Ovchinnikov, V. I. Kuznetsov, B. T. Porodnov, et al., The Contribution from Surface Diffusion in Measurements on Effective Pore Diameters in Nuclear Ultrafiltration Membranes Made by Gas-Dynamic Methods [in Russian], Preprint 18-84-801, OIYaI, Dubna (1985).
14. P. Yu. Apel', Nuclear Tracks, 6, No. 2/3, 225-228 (1982).

15. A Method of Determining Filter Pore Radius [in Russian], Authors' Certificate (USSR) 1030701, IPC G 01 N 15/08.
16. V. I. Kunetsov, V. V. Ovchinnikov, V. D. Seleznev, and V. D. Akin'shin, Inzh. Fiz. Zh., 45, No. 2, 332-333 (1983).
17. Y. Shindo, T. Hakuta, H. Yoshitome, and H. Inoue, J. Chem. Eng. Japan, 16, No. 2, 120-126 (1983).
18. T. L. Hill, J. Chem. Phys., 25, No. 4, 730-735 (1956).
19. G. Klare and G. Rainish, Vysokomol. Soed., A21, No. 11, 2469-2485 (1979).
20. V. V. Ovchinnikov, V. I. Kuznetsov, B. T. Porodnov, et al., Abstracts for Heavy Ion Physics 85 [in Russian], R7-86-322, Dubna (1986).
21. Nguyen Nhu, Khodani-Joopari, H. Duscher, et al., An Experiment for Testing the Separation Efficacy for Gases of Hyperfine (<5 nm) Mica Tracks. GSI Scientific Report (1985).
22. I. E. Nikitina and Kh. I. Ismailova, Gas Processing and Gas Condensates [in Russian], Issue 4, pp. 3-15 (1976).
23. K. Kamide, S. Manabe, H. Makino, et al., Polymer J., 15, No. 3, 179-193 (1983).
24. R. A. W. Haul, Naturwiss, 41, No. 11, 255-256 (1954).
25. W. G. Trawick and A. S. Berman, J. Chem. Phys., 26, No. 2, 709 (1957).
26. K. Kammermeyer and D. D. Wyrick, Ind. Eng. Chem., 50, No. 9, 1309-1310 (1958).

RELAXATION IN A LOW-PERMEABILITY POROUS MATERIAL

O. Yu. Dinariev and O. V. Nikolaev

UDC 532.546

Relaxation in low-permeability porous materials has been examined for nonstationary infiltration.

Darcy's law applies [1] to steady-state motion through an isotropic porous material under a low pressure gradient, which relates the flow speed **u** to the pressure p and the gravitational potential φ:

$$\mathbf{u} = -\frac{k}{\mu}\nabla G, \quad G = p + \rho\varphi. \tag{1}$$

(1) must be modified on a relaxation model for nonstationary infiltration [2, 3]. If **u** and G are variable in time, (1) is replaced for a homogeneous isotropic porous medium by

$$\mathbf{u}(t) = -\frac{k}{\mu}\int_{-\infty}^{+\infty} K(t-t_1)\,\nabla G(t_1)\,dt_1, \tag{2}$$

in which the kernel K(t) is independent of the spatial coordinates and satisfies the conditions: K = K(t) is a function of time with dimension 1/time, possibly generalized, $\int_{-\infty}^{+\infty} K(t)dt = 1$, and the support for K = K(t) by virtue of causality lies on the $[0, +\infty)$ semi-axis.

If one performs a Fourier transformation with respect to t for the functions in (2), one gets

$$\mathbf{u}(\omega) = -\frac{k}{\mu}\tilde{K}(\omega)\,\nabla G(\omega), \tag{3}$$

in which the complex function $\tilde{K}(\omega)$ is such that

$$\tilde{K}(0) = 1, \quad \overline{\tilde{K}(\omega)} = \tilde{K}(-\omega). \tag{4}$$

For small ω, the simplest approximation for $\bar{K}(\omega)$ compatible with (4) is the linear one:

All-Union Natural Gas Research Institute, Moscow. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 58, No. 1, pp. 78-82, January, 1990. Original article submitted September 23, 1988.