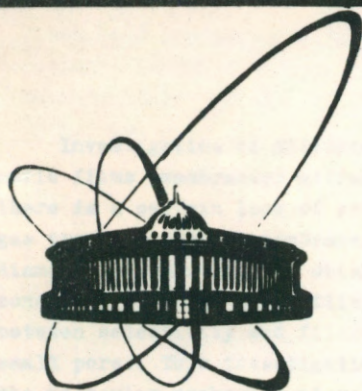


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ОБЪЕДИНЕННЫЙ  
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INVESTIGATION OF SEPARATION EFFICIENCY  
FOR GASES ON NUCLEAR MEMBRANE  
WITH HYPERFINE PORES

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## 1. INTRODUCTION

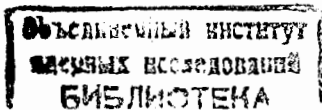
Investigation of diffusion of gas mixtures through various polymeric films (membranes) attracts great attention <sup>/1-4/</sup>. However, there is a certain lack of scientific information on the problem of gas transfer through membranes with small pores (less than 10 nm in diameter). Importance of obtaining such information is, first of all, connected with the possibility of attaining optimal correlation between selectivity and filtration productivity of the membranes with small pores. This investigation has been made in the hope to find out the molecular mechanism of gas diffusion through the membranes with hyperfine pores<sup>\*</sup>.

Membranes with small pores are traditionally obtained by wet or dry formation of a polymeric film. In this way, for example, cellulose acetate membranes with pores 2.5-4 nm are made <sup>/5/</sup>. However, interpretation of results obtained on such membranes is difficult because of uncertainty of geometrical structure of channels. In this connection porous media having (if it is possible) pores of regular geometry are more preferable. So-called nuclear membranes, which are widely used in various branches of science, technology and every day life, belong to this class of materials <sup>/6-8/</sup>. These unique in their structure membranes are obtained by irradiation of thin (5-10 nm) polymeric films by fission fragments in nuclear reactors or by bombardment by heavy charged particles in accelerators with subsequent chemical treatment. At that, the most regular geometry of pores is attained by the latter method <sup>/8/</sup>.

Methods of obtaining nuclear membranes on the basis of polycarbonate and polyethylene terephthalate (PET) films with pore size from several thousands to 1-2 nm have been worked out at present. Of special interest are the membranes with pores less than 10 nm. In this case channel dimensions are comparable with characteristic dimensions of molecular interaction potentials and there arise phenomena essentially influencing on the selective permeability to gases.

The aim of the present work is the investigation of inert gases separation effectiveness by nuclear PET membranes with hyperfine

\*The results of this work were presented at the International Symposium on Membranes for Gas and Vapor Separation, Suzdal (USSR), Feb. 27-March 5, 1989. Abstract p. 112.



pores prepared by two different methods. The experimental data are interpreted on the basis of a theoretical model considering structural peculiarities of membranes, surface flows of non-localized adsorbed gas molecules and carrying-effects between the adsorbed molecular layer and the gaseous phase.

## 2. EXPERIMENT

### 2.1. Control apparatus of membrane permeability to gases

Measurements of nuclear PET membranes permeability to one-component gases were made on the experimental apparatus with piston and manometrical methods of gas flow determination. Principal schemes are given in Figs. 1 and 2, respectively.

Apparatus for membranes with the partly healed porous structure is shown in Fig. 1. Gas under pressure 0.0133 MPa (registered by vacuum gage 9) flowed through the nuclear membrane 13 into the vacuum part of chamber 11. The volume flow in the range  $(10^{-5}-2 \cdot 10^{-6}) \text{ m}^3/\text{s}$  was measured by a piston gas flow meter 6. The constant pressure in front of the membrane created by the movement of the piston was checked by the capacitive micromanometer 3 (sensitivity  $4 \cdot 10^{-3} \text{ Pa/C.p.s.}$ ) with the closed by-pass 5. The design of the capacitive micromanometer is described in <sup>19</sup>. Gas pumping was made by the adsorption pump 19.

Investigation of the gas flow through the nuclear PET membranes obtained by the freeze-dried method was performed on the apparatus with the manometric scheme of gas flow measurement, Fig. 2. Gas in chamber 3 at a given pressure flows through the membrane 8 into the previously vacuumed and measured volume 10. The rate of pressure increase in this volume was registered by the capacitive micromanometer 15 (sensitivity  $3 \cdot 10^{-4} \text{ Pa/C.p.s.}$ ) whose output signal was communicated onto the input of the frequency meter 16. To automatize the process of measurement micro-computer 18 was used. Vacuum in the working units of the device was created by the backing pump 27, diffusion pump 23 and vapor trap 21.

### 2.2. Permeability Measurement Method

According to the piston scheme of the gas flow measurement (Fig. 1), after opening the plug 12 in the chamber 11, gas at a certain drop of pressure flows through the membrane 13 into the vacuum. The volume of the chamber 11 was chosen rather large ( $\sim 1500 \text{ ccm}$ ). The compensation of the gas pressure decrease in front of the membrane was made by a slow-speed movement of the piston. Pressure was kept

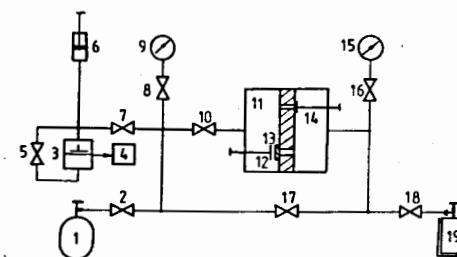


Fig. 1. Schematic view of experimental apparatus with piston gas flow-meter. 1 - pressurized container; 2, 7, 10, 17, 18 - valves; 3 - capacitive micromanometer; 4 - frequency meter; 5 - by-pass valve; 6 - measuring cylinder of piston gas flow meter; 8, 16 - manometer valves; 9 - manometer; 11 - chamber; 12 - valve of nuclear membrane; 13, 14 - by-pass muff; 15 - vacuum gage; 19 - adsorption pump.

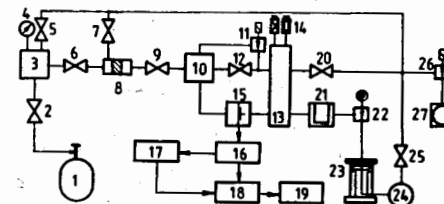


Fig. 2. Lay-out of experimental apparatus with manometric method of gas flow measurement. 1 - pressurized container; 2, 5, 6, 7, 9, 20, 25 - valves; 3 - pressure chamber; 4 - manometer; 8 - chuck with membrane; 10 - measuring volume; 11 - electromagnetic valve; 12 - by-pass valve; 13 - high vacuum chamber; 14 - thermocouple and ionization transformers; 15 - capacitive micromanometer; 16 - frequency meter; 17 - block of time intervals; 18 - computer; 19 - printer; 21 - vapor trap; 22 - valve with electromagnetic drive; 23 - diffusion pump; 24 - vacuum chamber; 26 - electromagnetic valve; 27 - backing pump.

constant with an accuracy to  $\pm 0.5\%$ . The valve of the volume flow through the membrane was determined as:

$$Q = \frac{\pi D^2 \Delta l}{4 \Delta t} \quad (1)$$

where  $D$  is the piston diameter,  $\Delta l$  is the value of the piston movement during the time  $\Delta t$ .

According to the manometric method of gas flow measurements (Fig. 2), it is necessary to watch the pressure increase in the volume 10. The main difficulty of these measurements is in determining the value of the volume 10, the expression for the gas volume flow contains

$$Q = \frac{\Delta P}{\Delta t} \frac{V}{P_0} \quad (2)$$

where  $\Delta P/\Delta t$  - is the rate of the pressure increase in the chamber 10;  $V$  is the volume of the chamber 10;  $P_0$  is the gas pressure in front of the membrane.

In this connection it turned out to be useful to measure the rate of the pressure increase in the volume 10 when helium flows into it through a glass capillary of a known geometry (tangential impulse accommodation coefficients of gas molecules on the surface of PET membrane pores and that of glass capillaries within the experimental error coincide <sup>/10/</sup>). As a result, the following expression was obtained

$$Q = Q^* \frac{P^*}{P} \left( \frac{\Delta P}{\Delta t} \right) \left( \frac{\Delta t}{\Delta P} \right)^* \quad (3)$$

(here the parameters relating to the capillary are marked by \*).

All experiments (Figs. 1 and 2) were made at pressures which satisfy the Knudsen law for the given membrane:

$$Q = \frac{1}{12} \frac{\pi d_{ef}^3}{l} V_t \frac{2-\epsilon}{\epsilon} \frac{\Delta P}{P_0} N \quad (4)$$

where  $d_{ef}$  and  $l$  are the effective gas dynamic diameter of pores and membrane thickness;  $\Delta P$  is the pressure drop;  $N$  is the total number of pores;  $\epsilon$  is the part of molecules diffusively reflected from the pore walls - tangential impulse accommodation coefficient.

According to this the mean effective diameter of the nuclear membrane pores was determined by experimental values of helium flow using exp. (4). Experiments on the permeability to hydrogen, nitrogen, krypton, xenon (relative to helium) were performed on gases with purity ~ 99.99% at room temperature.

### 2.3. Obtaining of nuclear PET membranes with hyperfine pores

PET film samples about 10  $\mu\text{m}$  thick irradiated by  $^{132}\text{Xe}$  ions with the energy ~ 1 MeV/nucleon, were placed into a conductometric

cell with solution 0.1 H NaOH at 80°C in it. In the process of etching the electroconductivity of the cell with membrane was registered continually. Effective pore size was evaluated by the conductivity value <sup>/11/</sup>. To avoid capillary contraction of pores less than 15 nm in the process of drying the samples were impregnated with easily volatile organic liquids chosen experimentally and dried in freeze-dried way. Nuclear PET membranes with effective pore size up to 2 nm were obtained in this way.

According to another method nuclear membranes were etched up to pore diameters 15-20 nm and dried in a usual way. Then the samples were placed in a closed container and kept there for a long time. At that gradual healing of PET membrane pores under the action of Laplas tensions occurred on the curved channels surface. The final size of pores for some samples was 2-3 nm. To obtain pores of the necessary size the healed membranes were subjected to periodical pressure loading leading to the growth of pores with subsequent unloading according to the method described in <sup>/12/</sup>.

The working surface of membranes was  $(0.71 \pm 0.03) 10^{-5}$  sq.m and  $(0.95 \pm 0.02) 10^{-4}$  sq.m for freeze-dried membranes and for those with a partly healed structure, respectively. The pore density evaluated by the electron microscopic analysis is  $(3.2 \pm 0.4) 10^{-12}$  1/sq.m and  $(4.8 \pm 0.6) 10^{12}$  1/sq.m (sample 1);  $(4.2 \pm 0.5) 10^{12}$  1/sq.m (sample 2) for two various ways of obtaining membranes with hyperfine pores.

### 2.4. Measurement results

In the experiments volume flows of one-component gases  $Q_i$  in the Knudsen regime of flow were measured. By the values of  $Q_i$  the relative gas flow was determined as

$$\omega_{ij} = \frac{Q_i}{Q_j} \left( \frac{M_i}{M_j} \right)^{0.5} \quad (5)$$

where  $M_i, M_j$  are molecular masses of investigated gases.

To describe membrane separative characteristics, the ideal separation coefficient is usually used

$$\alpha_{ij} = \frac{Q_i}{Q_j} \quad (6)$$

Thus, one can conclude that  $\omega_{ij}$  is the ideal separation coefficient of gases  $i$  and  $j$  relative to the theoretical Knudsen value.

The experimentally obtained values  $\omega_{ij}$  depending on the effective pores diameter  $d_{ef}$  of the membranes prepared by two different methods are given in Fig. 3. Here one can see that for the membranes

with  $d_{ef} > 5-6$  nm  $\omega_{ij}$  tends to 1, which corresponds to Knudsen gas flow inside the pore space. With a gradual decrease of pore size the relative ideal separation coefficient drops for the majority of gas pairs. The given phenomenon can be qualitatively described within the framework of standard "jump" diffusion model for gas molecules on the channel surface <sup>/13/</sup>. With the help of this model one can explain the small growth of the coefficient  $\omega_{ij}$  of the pair hydrogen-helium for the membranes obtained by the freeze-dried method with  $d_{ef} \approx 2$  nm.

However, one can see other experimental results as well. Thus, with the decrease of pores size in the membranes with the partly healed structure the effectiveness of separation grows for pairs helium-nitrogen and helium-argon. Besides, Fig. 3 shows that the values for pairs helium-nitrogen and helium-xenon on the membranes obtained by different methods do not conform. On the freeze-dried membranes there is a decrease of  $\omega_{ij}$ , whereas on the membranes with partly healed pores there is a growth. As it will be shown later, these differences can be interpreted on the basis of the kinetic approach in the consideration of gas flows in hyperfine pores.

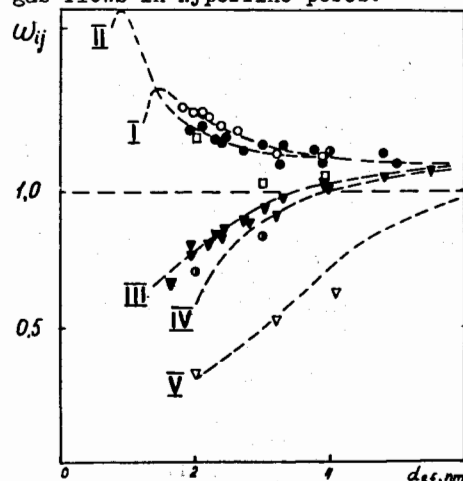


Fig. 3. Dependence of the relative ideal coefficient on the effective gas dynamic pore diameter: O, ●, ▽ (1,2,3) for the membranes with partly healed pores; ○, ▽, □ (4,5,6) for freeze-dried membranes; the gas pairs: helium-nitrogen - 1 and 4; helium-xenon - 3 and 5; helium-argon - 2; hydrogen-helium - 6; curves I, III and II are obtained for the pairs helium-nitrogen, helium-xenon and helium-argon on the basis of exp. (19); curves IV and V are obtained for the pairs helium-nitrogen and helium-xenon according to exp. (22).

### 3. THEORY

Consider in detail the processes of gas transfer through a single cylindrical channel with diameter  $d \approx d_{ef}$  which satisfactorily corresponds to the structure of the membranes with partly healed pores. As shown in <sup>/14/</sup>, the flows of free  $I_f$  and adsorbed  $I_a$  gas molecules through an arbitrary channel cross-section can be represented as:

$$I_f = -\alpha_{ff} \frac{1}{n_f} \frac{\partial n_f}{\partial x} - \alpha_{fa} \frac{1}{n_a} \frac{\partial n_a}{\partial x} \quad (7)$$

$$I_a = -\alpha_{af} \frac{1}{n_a} \frac{\partial n_f}{\partial x} - \alpha_{aa} \frac{1}{n_a} \frac{\partial n_a}{\partial x}$$

where  $n_f$  and  $n_a$  are densities of free and adsorbed molecules;  $\alpha_{kr}$  are kinetic coefficients.

Here one supposes that the flow  $I_a$  consists of non-localized adsorbed gas molecules, and the collisions among molecules in phases a and f can be neglected. The cross kinetic coefficients  $\alpha_{fa} = \alpha_{af}$  describe isothermal carrying-effects <sup>/14/</sup> and are due to the fact that the tangential impulse transfer between phases a and f takes place during adsorption and desorption of molecules.

Localized molecules do not take part in the transfer process directly. Their influence can be seen only at a high degree of surface filling by heavy gases at sufficiently low temperatures, when the scattering of mobile gas molecules occurs not on the polymer macromolecules of the membrane, but on the tightly bounded (localized) gas molecules.

A large channel length ( $l/d > 10^3$ ) and a small pressure drop allow one to consider that in any element of the channel length sufficiently distant from the ends there is local equilibrium between the gaseous and adsorbed phases. In this case:

$$\frac{1}{n_f} \frac{\partial n_f}{\partial x} = \frac{1}{n_a} \frac{\partial n_a}{\partial x} = \frac{\Delta P}{LP_0} \quad (8)$$

The total molecule flow  $I$  through the channel cross-section is

$$I = I_f + I_a = (\alpha_{ff} + 2\alpha_{fa} + \alpha_{aa}) \frac{\Delta P}{LP_0} \quad (9)$$

The kinetic coefficient  $\alpha_{ff}$  can be written as <sup>/14/</sup>:

$$\alpha_{ff} = \frac{1}{4} n_f V_f S_f \lambda_f \quad (10)$$

where  $S_f$  is the cross-sectional area of the channel;  $V_f$  is the mean thermal velocity;  $\lambda_f$  is the characteristic relaxation length of free molecules in the channel.

We consider <sup>/17/</sup> that the total energy of gas particles is essentially changed only as a result of their inelastic collisions with polymer atoms. Then the existence of a potential well close to the channel surface leads to the distortion of  $\lambda_f$  and to the decrease of the effective flow area  $S_f$ . Indeed, the number of free molecules incident on the unit of channel surface in the unit of time with the velocity near  $\vec{V}$  is equal to  $V_n f(\vec{V}) d^3 V$  (here  $f(\vec{V})$  is the velocity distribution function of gas molecules  $d^3 = dV_x dV_y dV_z$ ). At the movement of gas molecules in the potential well of characteristic depth  $U$  with conservation of total energy, their normal velocity increases, i.e.,  $V'_n = (V_n^2 + 2U/m)^{0.5}$  ( $m$  is the molecular mass). The flow of particles nevertheless remains constant. Thus,

$$V'_n f(\vec{V}') d^3 V' = V_n f(\vec{V}) d^3 V.$$

According to the law of energy conservation  $V'_n d^3 V' = V_n d^3 V$ . Then it follows from (11) that  $f(\vec{V}') = f(\vec{V})$ . Whereas at a slight difference of the system from the equilibrium state it means

$$n'_f = n_f \tau, \quad (12)$$

where  $n'_f$  is the density of free gas molecules in the range of static attraction potential  $U$  influence;  $k$  is the Boltzman constant;  $T$  is the absolute temperature;  $\tau = \exp(U/kT) \cdot \text{erfc}(U/kT)^{0.5}$ .

Let the surface potential have a form of a rectangular well with the width  $h/2$ , and gas molecules be hard spheres with diameter  $d_g$ . Thus, the characteristic length of the gas molecules path  $d^*/2$  in the surface potential field is less than  $h/2$  by the sum of characteristic thickness of localized layer  $\Delta/2$  and the value of molecular radius  $d_g/2$  (Fig. 4).

Thus,

$$d^* = h - (d_g + \Delta). \quad (13)$$

Then for  $\alpha_{ff}$  one can write the following expression:

$$\alpha_{ff} = C_{ff} (d-h)^2 (d-h+h^*) n_f V_f \quad (14)$$

$$C_{ff} = \frac{\pi}{12} \frac{2-\varepsilon}{\varepsilon} \left(1 + \frac{2d^*(d-h)+d'^2}{(d-h)^2} \tau\right), \quad h^* = d^* \tau.$$

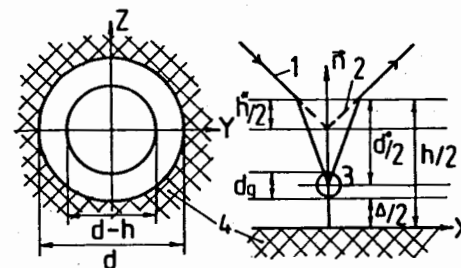


Fig. 4. Motion of gas molecules in the potential field of the membrane channel surface. 1 - real trajectory; 2 - effective trajectory, 3 - gas molecule; 4 - channel surface

Surface flow of unlocalized adsorbed molecules is determined by the coefficient <sup>/14/</sup>:

$$\alpha_{aa} = \frac{1}{4} n_a V_f S_a \lambda_a, \quad (15)$$

where  $n_a$  is the density of unlocalized molecules;  $S_a$  is the cross-sectional area of the circular region of their flow;  $\lambda_a$  is the characteristic relaxation length of adsorbed molecules.

Let  $E$  be the characteristic value of the potential barriers preventing the movement of adsorbed gas molecules along the surface. Then the value of density  $n_a$  with  $E < U$  can be evaluated by <sup>/15/</sup>:

$$n_a = n_f \left( \exp\left(\frac{U-E}{kT}\right) - 1 \right). \quad (16)$$

Considering that  $\lambda_a \approx C_a d^*$  (here  $C_a$  is the constant), we obtain

$$\alpha_{aa} = \frac{\pi}{16} C_a d^{*2} (2(d-h) + d^*) \left( \exp\left(\frac{U-E}{kT}\right) - 1 \right) n_f V_f. \quad (17)$$

Since the characteristic energy of unlocalized adsorptive states of gas molecules is more than that of localized states by the value  $E$ , one can expect that desorption and adsorption of gas molecules are mainly realized by more probable transitions between the free and unlocalized states. In this case for cross kinetic coefficients  $\alpha_{fa} = \alpha_{af}$  using the estimation <sup>/14/</sup>, we get

$$\alpha_{fa} = C_{ff} C_a (d-h)^2 d^* \beta n_f V_f, \quad (18)$$

where  $\beta$  is the adsorption probability at a given temperature.



Thus, the relative ideal separation coefficient of any gas with regard to helium for membrane consisting of  $N$  identical channels with diameter  $d$  can be written in the following form:

$$\omega_{g-He}^0 = \frac{I_g}{I_{He}} \left( \frac{m_g}{m_{He}} \right)^{0.5} = A(1 - h'/d_0)^3 + \quad (19)$$

$$\frac{B}{d_0} (1 - h'/d_0)^2 + \frac{C}{d_0^2} \left( 1 - \frac{h' - d^*/2}{d_0} \right),$$

where  $d_0 = d - d_{He}$  is the gas dynamic pore diameter by helium;  $d_{def} = d_0$ ;

$$A = \alpha \left[ 1 + \frac{2d^*(d_0 - h) + d^{*2}}{(d_0 - h)^2} \exp\left(-\frac{U}{KT}\right) \right]; \quad \alpha = \left( \frac{2 - \epsilon_g}{\epsilon_g} \right) \left( \frac{\epsilon_{He}}{2 - \epsilon_{He}} \right);$$

$$B = 2A(h^* + \beta C_a d^*); \quad C = \frac{3}{2} \left( \frac{\epsilon_{He}}{2 - \epsilon_{He}} \right) C_a d^{*2} \left[ \exp\left(\frac{U - E}{KT}\right) - 1 \right].$$

To obtain (19) we supposed that helium is not practically adsorbed on the channel surface at room temperature <sup>/13/</sup>.

The given theoretical approach, first of all, relates to the membranes with partly healed regular pores. The membranes obtained by the freeze-dried method are characterized by different values of the separation coefficient and, therefore, such a simplified model fails.

One can suppose that in this case a circular sponge structure with pores of  $d_s \leq h$  in diameter is formed around each cylindrical channel. Such a structure can be formed at such etching times when the diameter  $d_0$  of the channel does not exceed the diameter  $d_{sm}$  of the radiation damages region formed at irradiation of the PET film by heavy ions.

If the etching process is stopped earlier the possibility of obtaining the sponge structure in the track core is not excluded.

Most probably the occurrence of the sponge structure can be expected not along the whole length of the track, but only in its inner regions.

Suppose that the external diameter of a sponge structure is  $d_{sm}$ . In this case in (9) there appears an additional term  $I_s$ :

$$I_s = -\alpha_{SS} \frac{1}{n_s} \frac{\partial n_s}{\partial x} = \alpha_{SS} \frac{\Delta P}{LP_0}, \quad (20)$$

where  $n_s$  is the density of gas molecules in the pores of sponge structure ( $n_s \geq n_a$ ).

The kinetic coefficient  $\alpha_{SS}$  has the following form:

$$\alpha_{SS} = \frac{1}{4} n_s \gamma_s S_s \lambda_g V_f, \quad (21)$$

where  $S_s = \frac{\pi}{4} (d_{sm}^2 - d_0^2)$  is the cross-sectional area of the circular sponge region;  $\gamma_s$  is the nondimensional permeability coefficient equal to the ratio of the section area of the sponge structure pores to its total section area;  $\lambda_g$  is the characteristic relaxation length of gas molecules in the sponge structure pores.

With  $d_0 > d_s$  the additional term  $I_s$  in (9) and (19) leads to the expression for the relative ideal separation coefficient in the form

$$\omega_{He-g} = \left( \frac{\omega_{g-He}^0 + F_g/d_0 ((d_{sm}/d_0)^2 - 1)}{1 + F_{He}/d_0 ((d_{sm}/d_0)^2 - 1)} \right)^{-1}, \quad (22)$$

where

$$F_g = \frac{3}{4} \frac{\epsilon_{He}}{2 - \epsilon_{He}} \frac{n_s}{n_f} \gamma_s \gamma_g, \quad F_{He} = \gamma_s d_s.$$

Here the values  $d_0$  corresponding to the experimental values are determined from the equation

$$d_{def}^3 = d_0^3 \left( 1 + F_{He}/d_0 ((d_{sm}/d_0)^2 - 1) \right). \quad (23)$$

With  $d_0 \leq d_s$  the relative separation coefficient does not depend on  $d_0$ :

$$\omega_{He-g} \approx F_{He}/F_g.$$

#### 4. INTERPRETATION OF EXPERIMENTAL RESULTS AND DISCUSSION

The analytic expressions obtained for the separation coefficients were used to treat the experimental data. Exp. (19) was used to interpret the functions  $\omega_{ij}^0(d_0)$  for the gas pairs: helium - argon, helium - nitrogen and helium - xenon obtained on the membranes with partly healed channels. In the general case exp. (19) includes unknown parameters  $d^*$ ,  $h'$ ,  $d$ ,  $\beta$ ,  $C_a$ . However, the coefficient  $d$  can be easily found in the extreme case  $\omega_{ij}^0 \approx d$  with  $d_0 \gg h'$ . Thus,  $d = 0.92$  with  $\epsilon_{He} \approx 0.96$  and  $\epsilon \approx 1$  (determined experimentally) for the rest of gases. For gases with a small degree of the surface filling by molecules the thickness of the unlocalized molecules flow region is a maximum and equal to  $d^* = h' - (d_g - d_{He})$ .

Figure 3 shows the theoretical curves approximating the experimental data (points 1, 2 and 3) by the least squares method (LSM) with three fitting parameters. For each gas, considering the evaluation of the surface filling degree, the value  $h - d^*$  was found beforehand and the value  $\alpha = 0.92$  was set <sup>/10/</sup>. Gas molecule diameters were taken from paper <sup>/16/</sup>:  $d_{He} = 0.18$  nm,  $d_{Ar} = 0.27$  nm,  $d_{N_2} = 0.32$  nm,  $d_{Xe} = 0.32$  nm.

At room temperature the degree of surface filling by argon and nitrogen molecules is negligibly small. For these gases physically non-contradictive parameters  $h$ ,  $\beta$ ,  $C_a$  and  $C$  are obtained at the minimal value  $h - d^* = d_g - d_{He}$  ( $\Delta = 0$ ). The degree of filling of localized states at the same conditions for xenon, on the contrary, is close to 1. The fact that the values  $h$  obtained as a result of the experiment treatment are negative with  $h - d^* < 0.25$  nm proves it. The value  $h - d^* = 0.4$  nm ( $\Delta = 0.257$  nm) is taken on the assumption of the full filling of the localized adsorption centers forming a two-dimensional periodic lattice with a spacing  $\delta \approx 1$  nm <sup>/13/</sup>. The calculation results are given in Table 1.

The first term in exp. (19) dominates with  $d_0 \gg h$ , the last one with  $d_0 \leq 0.5$ . The maximum contribution of the second term is in the intermediate region of pore size and equals 0.65 with  $d_0 \sim 1.6$  nm for argon; 0.65 with  $d_0 \sim 2.4$  nm for nitrogen and 0.3 nm with  $d_0 \sim 2.9$  nm for xenon.

The contribution about 80% to the value of coefficient B is made by the isothermal carrying-effects among free and non-localized adsorbed gas molecules (Table 1). It follows from the expression for coefficient B that the carrying-effects do not depend on the density of nonlocalized gas molecules but are determined only by their mean macroscopic velocity along the surface (through Clausing

Table 1

The main gas-permeability parameters of nuclear membranes with partly healed porous structure

Parameters	Argon	Nitrogen	Xenon
$h$ , nm	0.97	1.35	1.26
$d^*$ , nm	0.69	1.03	0.68
$\beta C_a$	1.23	1.39	1.59
$U$ , kcal/mol	2.4	2.8	8.0
$U-E$ , kcal/mol	0.12	0.15	1.13

factor  $C_a d^*/L$ ) and by a part  $\beta$  of the desorbed molecules in the gas flow reflected by the surface. On the contrary (see exp. (19)), the contribution of the surface flow to  $\omega_{g-He}^0$  essentially depends on the density  $n_a$  and is very sensitive to the barrier heights  $E$  in comparison with the well depth  $U$ .

The competition of three mentioned contributions to the total gas flow through the membrane leads to the appearance of a local maximum in the function  $\omega_{ij}^0(d_0)$  for the pairs helium-argon, helium-nitrogen (curves 1, 2 in Fig. 3) and a minimum for the pair helium-xenon (curve 3) in the region  $d_0 \sim 1.0-1.5$  nm. With further decrease in the diameter strong distortion of the potential field inside the channels appears and exp. (19) fails.

To describe the gas transfer in the membrane obtained by the freeze-dried method exp. (22) derived on the assumption of the existence of a sponge structure inside the track was used.

The treatment was performed by the LSM-method with three fitting parameters  $d_{sm}$ ,  $F_g$  and  $F_{He}$ . The values for  $\omega_{g-He}^0(d_0)$  are taken from the experiments on the membranes with a partly healed structure. The calculation results are given in Table 2, and the curves are shown in Fig. 3 (for points 4 and 5).

Table 2 shows that the sponge region characteristics  $d_{sm}$  and  $F_{He}$  in exp. (22) do not depend on the kind of gas according to the theoretical model within the experimental error. On the contrary, the coefficient  $F_g$  increases with the growth of molecular weight of an investigated gas. The obtained values of  $d_{sm}$  satisfactorily agree with the data of other authors about the size of the radiation damage region <sup>/11/</sup>. It is worth noting that exp. (23) at the above-mentioned values  $F_{He}$  and  $d_{sm}$  has a solution  $d_0 \approx d_s$  (the separate central channel does not exist, the sponge structure occupies the whole track region) even with  $d_{def} \approx 2.1$  nm. That is why the obtaining of freeze-dried membranes with  $d_{def} < 2$  nm is impossible without essential

Table 2

Gas-permeability parameters of nuclear membranes prepared by the freeze-dried method

Parameters	Nitrogen	Xenon
$d_{sm}$ , nm	17.2	17.9
$F_g$ , nm	0.48	1.12
$F_{He}$ , nm	0.3	0.34



change in technology. From this point of view the method of partial pores healing after etching of the sponge structure is more perspective.

Influence of the sponge structure in nuclear membranes on separation of various gases is seen from the curves in Fig. 3. With the decrease of pore size the separation coefficient of the pairs helium-nitrogen (curve IV) and helium-xenon (curve V) drops. It is connected with a high value of the sum  $l_a$  and  $l_f$  in the flow  $l$  for a heavier gas. The similar behaviour for the pair helium-xenon (curve III) is also observed for the membranes with partly healed pores because of the high value of  $l_a$  for xenon. Nevertheless, the absence of the sponge structure here does not lead to such a strong decrease in the coefficient  $\omega_{ij}$  ( $l_s = 0$ ).

The observed increase in  $\omega_{ij}$  in the experiments on the membranes with partly healed pores for the pairs helium-nitrogen and helium-argon (curves I and II), respectively, is due to the above-mentioned mechanism of decreasing the effective cross sectional area for a free flow of heavy gas under the influence of the static potential field in the channel. In this case the decrease in flow  $l_f$  is not compensated for by the growth of  $l_a$ , therefore the separation effectiveness increases. The calculation gives the maximum relative ideal coefficient of gas separation for the pair helium-nitrogen  $\omega_{ij}^0 \sim 1.4$  with  $d_0 \sim 1.5$  nm, whereas for the pair helium-argon  $\omega_{ij}^0 \sim 1.5$  nm, with  $d_0 \sim 1$  nm. Thus, unlike freeze-dried membranes, where  $\omega_{ij}$  lowers with decreasing (curve III), the gas separation coefficient of the membranes with partly healed structure grows and reaches the maximum (curve I).

Note that the given effect cannot be satisfactorily described within the framework of the model suggested in /18/. According to /18/, there is an effective relaxation mechanism in the potential well region for heavy gases. It leads to the fact that densities of free gas particles outside the well and inside it are practically equal (unlike, e.g. exp. (12)).

Besides, on the membranes obtained by the freeze-dried method we can observe the growth of  $\omega_{ij}$  with the decrease of  $d_0$  for the pair hydrogen-helium. The sponge structure is likely to play a positive role in the hydrogen transfer increasing its flow at the expense of  $l_s$ . Unfortunately, the absence of the experimental data on  $\omega_{H_2-He}^0(d_0)$  does not allow one to plot a corresponding theoretical curve for  $\omega_{H_2-He}$  and to evaluate the separation coefficients for  $d_0 < 2$  nm. One can only suppose that the values of  $\omega_{ij}$  for the pair hydrogen-helium for the membrane with partly healed pores turn

out to be less than for the samples dried by the freeze-dried method.

It should be added that etching of membranes up to  $d_0 > d_{sm}$  leads to the disappearance of the flow  $l_s$ . Thus, even with  $d_0 > 6.5$  nm the data on the membranes obtained by two different methods coincide within the experimental error.

#### CONCLUSION

Experimental investigation of the separation of a number of inert gases on nuclear membranes with hyperfine pores has shown that despite equal effective gas dynamic size of pores by helium, their gas selective properties essentially depend on the method of making the membranes.

So, it was found out that for the membranes obtained by means of partial healing of the porous structure smaller pore size (less than 6 nm) leads to a larger relative ideal coefficient for the pairs helium-argon and helium-nitrogen. For the membranes obtained by the freeze-dried method the corresponding separation coefficients decrease. According to other investigated gas pairs different membranes showed qualitatively similar results. These, at first sight, obvious contradictions in the experimental data cannot be explained by means of the traditional simplified approaches.

Consideration of surface effects from the kinetic point of view with taking into account structural peculiarities of the membranes, potential fields and isothermal carrying-effects between free and adsorbed gas molecules enabled us to get theoretical expressions not only explaining the obtained results but predicting gas selective properties of membranes with smaller pores (less than 2 nm).

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Исследование эффективности разделения газов на ядерных мембранах с ультрамалыми порами

Проведено экспериментальное исследование эффективности разделения ряда инертных газов /водорода, гелия, азота, аргона, криптона и ксенона/ на ядерных мембранах из полиэтилентерефталата с размерами пор менее 10 нм. Полимерные мембраны указанного диапазона пор могут быть получены как лиофильным способом, так и при частичном "залечивании" пористой структуры под действием лапласовских напряжений /капиллярная контракция/ с первоначально несколько большим размером пор. Обнаружено, что мембраны с диаметром пор большим 6 нм при нормальных условиях имеют идеальный коэффициент разделения газов близкий к теоретическому. Постепенное уменьшение размеров пор ведет к росту приведенного идеального коэффициента разделения пары гелий-водород для мембран, полученных лиофильным способом, и пар гелий-аргон и гелий-азот - для мембран с частично контрактировавшими порами. По другим исследованным парам газов наблюдалось падение коэффициентов разделения. Предложена теоретическая модель, позволяющая описать наблюдающиеся закономерности в рамках поверхностной диффузии компонентов с учетом изотермических эффектов межфазного увлечения.

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Investigation of Separation Efficiency for Gases at Hyperfine Nuclear Membranes

The experimental investigation was carried out of separation efficiency for a number of inert gases (hydrogen, helium, nitrogen, argon, krypton and xenon) on nuclear polyethyleneterephthalate membranes with a pore size smaller than 10 nm. Polymeric membranes with pore size shown can be manufactured both by the freeze-drying technique and by partially "healing" porous structure under the action of Laplace stresses (capillary contact from initially larger pore size). It was found that membranes with pore diameter larger than 6 nm under normal conditions have the ideal separation ratio for the gases at NTP close to the theoretical one. Gradual reduction of the pore size leads to the growth of the non-dimensional ideal separation ratio of hydrogen-helium pair for membranes made by the freeze-drying method and of the helium-argon and helium-nitrogen gas pairs for membranes with partially shrunk pores. For other gas pairs a decrease in separation coefficients was observed. A theoretical model is proposed which permits one to describe the observed behaviour within the framework of surface diffusion of components taking into account the isothermal interphase entrainment effects.

The investigation has been performed at the Laboratory of Nuclear Reactions, JINR.

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