EFFECTS OF THIN CARBON FILMS ON THE SELECTIVE GAS PERMEABILITY OF A POLYMER MEMBRANE

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Measurements have been made on the selectivity and gas permeability of a polyvinyltrimethylsilane (PVTMS) membrane bearing a thin carbon coating in the separation of gas mixtures containing CO_2 and O_2.

The performance in separating a gas mixture by diffusion using polymer membranes is dependent on the specific gas permeability and selectivity. These parameters determine the dimensions of the apparatus, the energy consumed, and the number of stages required to provide a given enrichment in the target component.

Unsymmetrical membranes have been made with thin separating layers having permeabilities higher by several orders of magnitude than those of homogeneous ones. For example, unsymmetrical membranes made of PVTMS are widely used in enriching air in oxygen, separating carbon dioxide from the atmosphere and enclosed volumes, etc. However, the selectivities of existing polymer membranes for CO_2 and O_2 are only a few units, which is inadequate for some purposes.

The permeability K and the selectivity α of a membrane for a binary A—B mixture are defined by [1]

$$K_A = qy\delta/\Delta p_A, \tag{1}$$

$$K_B = q(1-y)\delta/\Delta p^B, \tag{2}$$

$$\alpha = K_A/K_B, \tag{3}$$

where $\Delta p_A = P_{A(0)} - P_{A(K)} = P_0 x - P_K y$, $\Delta p_B = P_{B(0)} - P_{B(K)} = P_0(1-x) - P_K(1-y)$ are the differences in the partial pressures of the components in the retained and transmitted parts, which can be taken as follows when the penetrating part is evacuated under vacuum ($P_K \ll P_0$): $\Delta p_A = P_{A(0)} = P_0 x$, $\Delta p_B = P_{B(0)} = P_0(1-x)$.

It follows from (1)-(3) that the degree of enrichment in the target component is

$$y = \alpha\Delta p_A/(\alpha\Delta p_A + \Delta p_B) = (1 + \alpha(1-x)/x)^{-1}. \tag{4}$$

If the gas penetrates by diffusion, the flux density through the membrane is proportional to the difference of the concentrations in the surface layers $c_{i(0)} - c_{i(K)}$ and to the diffusion coefficient D:

$$q_i = \frac{D(c_{i(0)} - c_{i(K)})}{\delta}. \tag{5}$$

The component concentrations are proportional to the partial pressures over the membrane $c_i = \sigma_i P_i$, where the solubility coefficient σ_i in general is a function of the concentration $\sigma_i = f(c_i)$. If the conditions $P_K \ll P_0$ and $c_{i(K)} \ll c_{i(0)}$ are met, we can write $q_i = D\sigma_{i(0)} P_0 x/\delta$, and then α and y are expressed as

$$\alpha = D_A\sigma_{A(0)}/(D_B\sigma_{B(0)});\ y = (1 + D_A\sigma_{A(0)}/(D_B\sigma_{B(0)}))^{-1}. \tag{6}$$

This shows that a possible way of increasing the selectivity and degree of enrichment is to increase the ratio of the solubilities for the target gas $\sigma_A(0)$ and the inert gas $\sigma_B(0)$ in the surface layer on the inlet side. For example, in the separation of CO_2—O_2 mixtures,

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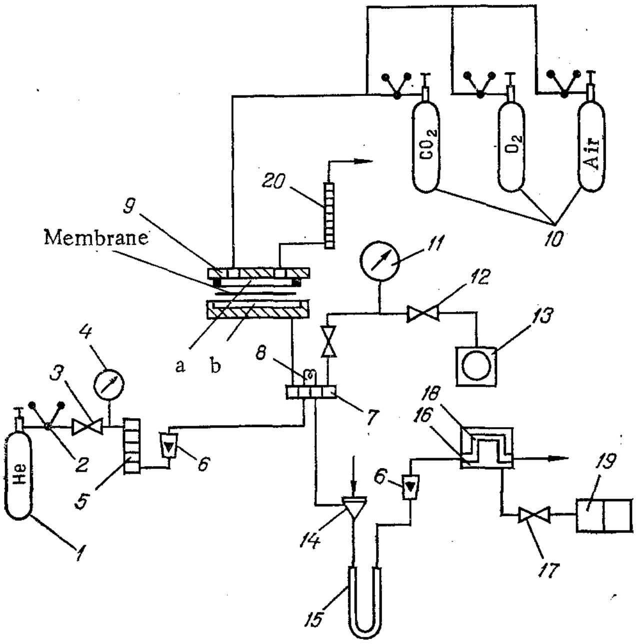

Fig. 1. Apparatus for determining the gas permeabilities of polymer membranes: 1) cylinder containing carrier gas (helium); 2) reduction valve; 3) control valve; 4) MT-4 gauge; 5) filter; 6) rotameter; 7) dispensing tap; 8) calibrated volume; 9) diffusion cell; 10) cylinder containing test gas; 11) standard vacuum gauge; 12) three-way stopcock; 13) VN-461 forevacuum pump; 14) inlet device; 15) packed column; 16) flow divider; 17) leak; 18) capillary tube; 19) MKh-1312 chromatographic-diffusion mass spectrometer; 20) foam flowmeters; a) inlet chamber; b) measurement chamber.

aluminum was deposited on the PVTMS membrane [2], which reduces the solubility of oxygen. The selectivity factor for the two-layer membrane was increased by a factor 2, but the overall gas permeability was substantially reduced.

As $\sigma_A(0)$, $\sigma_B(0)$ are dependent on the adsorption, it is possible [3] to modify the surface of a selective PVTMS membrane by depositing a carbon film on it. If the film has an appropriate structure, an increase in the solubility (adsorption capacities) ratio for CO_2 and O_2 by at least one and a half orders of magnitude is obtained by comparison with an uncoated PVTMS membrane.

The substrate was a homogeneous gas-separating membrane made of PVTMS of thickness 150-180 μm. An active carbon coating of thickness 500-700 Å was deposited by thermal evaporation under vacuum using a VUP-4 apparatus. The deposition was performed with the following parameters: vacuum in the working volume not lower than 10^{-5} Pa, total heater current 80 A, and deposition rate 6-20 Å/sec. A high vacuum is required in the working volume to obtain pure coatings not containing residual gases. The heater current was chosen at the above value because the deposition is more prolonged at lower levels and traces of residual gases affect the composition and performance of the coating. The coating thickness was varied by means of the deposition time. The optimum thickness was found to be 500 Å. A thickness less than 500 Å produced an insufficiently dense coating, and there was not substantial improvement in the selectivity, while thicker coatings (over 700 Å) represented barrier layers for carbon dioxide.

This two-layer membrane was tested with various gases in the apparatus whose block diagram is shown in Fig. 1.

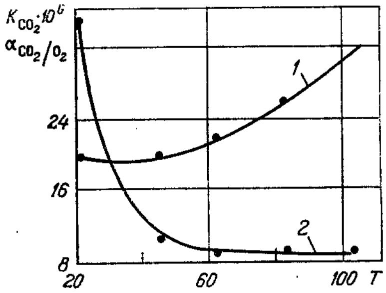

Fig. 2. Temperature dependence of the permeability 1 and selectivity 2.

TABLE 1. Values for the Permeability and Selectivity of PVTMS Membranes before and after Deposition of Carbon Films

Conditions	Specimen Nos.	Permeability, 10^6 cm^3/cm^2·sec·cm Hg			Selectivity	
		CO_2	O_2	air	CO_2 and O_2	CO_2 and air
Before deposition	1	21,32	3,55	—	6,1	—
	2	32,1	—	2,18	—	10,6
	3	19,63	—	1,64	—	12,0
	4	18,22	3,25	—	5,6	—
After deposition	1	3,27	0,07	—	48,0	—
	2	5,05	—	0,11	—	46,0
	3	2,01	—	0,054	—	37,0
	4	1,58	0,041	—	40,0	—

TABLE 2. Effects of Initial Mixture Composition on the Degree of Carbon Dioxide Enrichment in the Penetrating Gas

CO_2 content			Selectivity	
in initial mixture, x	in penetrating gas		before deposition, α_0	after depositions α'
	before deposition	after deposition		
12	37,3	68,4	6,1	48
8	26,9	40,9	5,6	40

The permeability and selectivity were determined from the accumulation of the penetrating gas in a chamber *a* of the diffusion cell 9, which was followed by qualitative analysis with an MKh-1312 chromatographic-effusion mass spectrometer. Inserts were used to seal the separating membrane into the diffusion cell. The inlet chamber *a* was supplied with the initial gas mixture at a slight excess pressure. The penetrating gas was removed from the space under the membrane by a vacuum pump.

We examined the extraction of carbon dioxide from $CO_2 + O_2$ mixtures with two different initial compositions, where the separating membranes were homogeneous PVTMS films with or without carbon.

The ratio of the amount of input mixture to the amount penetrating was kept at 10.

The results (Table 1) show that the selectivity is increased by about an order of magnitude by the carbon film. These results may be explained, as was suggested before the experiments were performed, by changes in the adsorption at the surface on interaction with the $CO_2 + O_2$ mixture, which causes an increase in the relative solubility of CO_2, namely $\sigma_{CO_2}/\sigma_{O_2}$, in the input layer. The exact effect is clearly dependent on the structural and geometrical parameters of the coating, as well as on the separation conditions (separation rate), the adsorption, the rates of passage of the gases through the membrane, etc. With this membrane, the relative increase in the surface solubility of CO_2 calculated from (6) was by a factor of 7-8 (Table 2). There was a certain reduction in the overall permeability, which was evidently due to the additional diffusion resistance represented by the deposited layer.

TABLE 3. Effects of Initial Mixture Pressure on Gas Flux Density through a Modified Membrane

Initial mixture pressure, atm	Gas flux density, 10^4 cm^3/cm^2·sec		Selectivity
	CO_2	O_2	CO_2/O_2
1	0,172	0,004	42,0
2	0,367	0,008	44,8
3	0,560	0,012	45,0
4	0,738	0,016	45,1
5	0,925	0,020	46,0

We also examined the effects of the pressure difference on the permeabilities for carbon dioxide and oxygen in the two-layer membrane containing an active carbon film. Table 3 gives the results, which show that an increase in pressure produces virtually no increase in $\sigma_{A(o)}$ for the coating for CO_2 or in α at least in the pressure range used, which is in agreement with the theory and with the adsorption isotherms for activated carbon.

Figure 2 shows how the CO_2 permeability coefficient and separation factor are dependent on temperature for PVTMS coated membranes. The permeability increases with temperature, as does the separation coefficient. The permeability varied over time but attained a steady value after a certain interval.

NOTATION

K, permeability coefficient; α, selectivity coefficient; q, density of penetrating mixture flow; x, y, volume concentrations in the nonpenetrating and penetrating mixtures; δ, membrane thickness; P_0, P_K, gas pressures before and after membrane; D, diffusion coefficient; σ, solubility coefficient; c_i, concentration in the subsurface layer.

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