MEMBRANE FILTRATION OF GASES. II.*

SEPARATION PROPERTIES OF SILICONE RUBBER AND POLYVINYLTRIMETHYLSILANE

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The phenomenological equations for the filtration of a two-component gas mixture through a membrane were derived. The filtration of O_2–N_2 mixture through the silicone rubber and polyvinyltrimethylsilane membranes was investigated experimentally. The experimental and calculated permeabilities at various concentrations were compared.

It was shown in previous paper[1] that air filtrated through the silicone rubber membrane is enriched by oxygen. In this work those results with new measurements (on thicker membrane) were compared each other. In addition the membrane prepared from polyvinyltrimethylsilane was investigated. The phenomenological equations were proposed for the quantitative description of the filtration process.

THEORETICAL

For the system containing k gaseous components which are exchanged with system environment in steady state at constant temperature and pressure we can write the phenomenological equation[2]

$$J_i = \sum_{j=1}^{k} L_{ij} F_j \,, \tag{1}$$

where J_i is flow of component i ($i = 1, 2, \ldots, k$); F_j is driving force, *i.e.* gradient of natural intensive variable; L_{ij} is phenomenological coefficient.

For the system exhibiting the mass flow only, the driving force can be expressed by the equation

$$F_j = \frac{d(-\mu_j/T)}{dx} \quad (\text{for } j = 1, 2, \ldots, k) \tag{2}$$

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and the chemical potential at low pressure by the relation

$$\mu_j = \mu_j^0(T, P) + RT \ln P_j \,, \tag{3}$$

where μ_j^0 is chemical potential of pure component j at temperature and pressure of the system, and P_j is partial pressure of the component j. After the differentiation of Eq. (2) at constant temperature we obtain

$$\frac{d(-\mu_j/T)}{dx} = -\frac{R \, d \ln P_j}{dx} = -\frac{R}{P_j}\frac{dP_j}{dx} \tag{4}$$

and then the phenomenological equation (1) can be written as

$$J_i = -\sum_{j=1}^{k}(L_{ij}R \, dP_j/P_j \, dx) \,. \tag{5}$$

Now, let us consider the two-component system, thus

$$\begin{aligned} J_1 &= -L_{11}(R \, dP_1/P_1 \, dx) - L_{12}(R \, dP_2/P_2 \, dx) \\ J_2 &= -L_{21}(R \, dP_1/P_1 \, dx) - L_{22}(R \, dP_2/P_2 \, dx) \,. \end{aligned} \tag{6}$$

By introducing the transport coefficients defined by the relation

$$K_{ij} = L_{ij}R/P_j \tag{7}$$

we obtain the equations

$$\begin{aligned} J_1 &= -K_{11}(dP_1/dx) - K_{12}(dP_2/dx) \\ J_2 &= -K_{21}(dP_1/dx) - K_{22}(dP_2/dx) \,. \end{aligned} \tag{8}$$

The total mass flow J is equal to the number of mol n passed through unit area (A) during unit time (t) under constant pressure gradient, *i.e.* $J = (1/A)(dn/dt)$. Let us call this flow the permeability which is determined by the expression

$$J = J_1 + J_2 = -K_{11}(dP_1/dx) - K_{12}(dP_2/dx) - K_{21}(dP_1/dx) - K_{22}(dP_2/dx). \tag{9}$$

Considering the Onsager reciprocity postulate on mixed phenomenological coefficients $(L_{ij} = L_{ji})$ and taking into the account the requirement of validity of Eq. (9) at limiting conditions (for pure components which implies $K_{12} = K_{21} = 0$) we can

TABLE I

Experimental and Calculated Permeabilities and Separation Factors of O_2–N_2 Mixtures

K_{11}, K_{12} (mol/atm cm s); x_0 is mole fraction of oxygen on high pressure side; J_{exp}, J_{calc} (10^{-9} mol/cm^2 s); $\Delta J = 100\,(J_{calc} - J_{exp})/J_{exp}$.

Silicone rubber $x = 0.0234$ cm $K_{11} = 0.286$ $K_{22} = 0.137$					Silicone rubber $x = 0.0672$ cm $K_{11} = 0.315$ $K_{22} = 0.152$					Polyvinyltrimethylsilane $x = 0.0154$ cm $K_{11} = 0.0597$ $K_{22} = 0.0135$				
x_0	α	J_{exp}	J_{calc}	ΔJ	x_0	α	J_{exp}	J_{calc}	ΔJ	x_0	α	J_{exp}	J_{calc}	ΔJ
0·000	—	5·38	5·38	0·0	0·000	—	2·09	2·09	0·0	0·000	—	0·81	0·81	0·0
0·143	2·05	6·68	6·18	−8·0	0·175	1·91	2·30	2·47	7·7	0·269	4·06	1·42	1·50	5·4
0·257	2·07	6·86	6·84	−0·4	0·280	2·02	2·51	2·70	6·9	0·322	3·96	1·55	1·64	5·6
0·303	2·00	7·17	7·11	−1·0	0·373	2·07	2·74	2·90	5·8	0·353	3·97	1·66	1·73	4·0
0·413	2·07	7·26	7·75	6·3	0·432	2·06	2·85	3·04	6·0	0·381	4·03	1·66	1·81	8·2
0·496	2·15	8·09	8·23	1·7	0·468	2·12	2·91	3·11	6·5	0·417	3·93	1·88	1·99	5·2
0·609	2·14	8·56	8·90	3·8	0·528	2·11	3·14	3·25	3·4	0·461	3·52	2·09	2·03	−2·7
0·705	2·17	9·55	9·48	−0·8	0·543	2·29	3·23	3·28	1·6	0·513	3·83	2·00	2·11	5·1
0·781	2·18	9·77	9·93	1·6	0·655	2·32	3·50	3·54	1·1	0·614	3·74	2·29	2·46	7·2
1·000	—	11·25	11·25	0·0	0·713	2·39	3·50	3·67	4·7	1·000	—	3·57	3·57	0·0
			Mean	2·3	1·000	—	4·33	4·33	0·0				*Mean*	4·3
								Mean	3·9					

write

$$J = -K_{11}(dP_1/dx) - K_{22}(dP_2/dx). \quad (10)$$

The transport coefficients K_{11} and K_{22} are the characteristic quantities for particular membrane material. The other characteristic property is the separation factor α_{12} defined by the relation

$$\alpha_{12} = x_1^l x_2^h / x_2^l x_1^h, \quad (11)$$

where x_i denotes mole fraction of the *i*-th component, superscript *h* denotes the high and superscript *l* the low pressure side of membrane.

EXPERIMENTAL

The equipment and the procedure were described in previous paper[1]. The experimental conditions were as follows: pressure drop on the membrane was 700 Torr, temperature 23 ± 1°C, area of membrane 32·0 cm^2 (please note that this value was misprinted in the paper[1]).

Materials. Silicone rubber membranes were prepared according to Barrer and Chio[3]. For the preparation of the polyvinyltrimethylsilane membrane the polymer was dissolved in cyclohexane first. Then this solution was poured on the surface of mercury and after complete evaporation of the solvent the membrane could be simply taken off. The gases for preparation of mixtures (oxygen and nitrogen) were of technical grade and were not purified.

RESULTS AND DISCUSSION

Separation factors, experimental and calculated permeabilities J (mol/cm^2 s) in dependence on mole fraction of oxygen on the high pressure side are summarized in Table I along with transport coefficients K_{11} and K_{22} (mol/atm cm s) and membrane thickness Δx (cm). The transport coefficients for the silicone rubber membranes are comparable each other within 10%. The enrichment factors of the polyvinyltrimethylsilane membrane are twice of those for silicone rubber but the rates of filtration are considerably slower.

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