Permselectivities through Artificial Membranes at a Non-steady State

AKON HIGUCHI and TSUTOMU NAKAGAWA, *Department of Industrial Chemistry, Faculty of Engineering, Meiji University, 1-1-1 Higashimita, Tama-ku, Kawasaki, Kanagawa 214, Japan*

Synopsis

Non-steady-state flux ratios of oxygen to nitrogen in a poly(dimethyl siloxane) membrane are theoretically investigated as a function of time. Concentration profiles of oxygen and nitrogen are found to decay to a negligible concentration with an increase of the distance from membrane surface and it is observed that oxygen penetrates deeper than nitrogen in the membrane at the non-steady state. Differences of concentration profiles of oxygen and nitrogen lead to enormously high selectivity for oxygen at the non-steady state. The flux and selectives are studied under the condition that the upstream pressure is pulsating to keep the non-steady state continuously as suggested by Paul [*Ind. Eng. Chem. Proc. Des. Dev.*, 10, 375 (1971)]. Model calculations are also performed for the concentration of uranium 235 from natural uranium. The flux ratio of uranium 235 to uranium 238 in the non-steady state is calculated to be 1.144 at time/L^2 = 800 s/cm^2 (L = membrane thickness), which is higher than the value, 1.00429, at a steady state.

INTRODUCTION

Artificial membrane processes (reverse osmosis, ultrafiltration, dialysis and gas separation) are mostly performed under steady-state conditions. The upstream pressures employed in industrial practice are commonly fixed with the only fluctuation being that arising from the motor used. In biological systems, on the other hand, mass transfer usually occurs under non-steady-state conditions. Breathing or blood transfer from the heart to other organisms is a pulsatile process. This is a non-steady-state condition since the pressure within a specific part is always changing as a function of time. On a more microscopic level, $Na^+ - K^+$ pumping in biological cells involves a flip-flop movement.[1] The flow of ions through a single channel in a biological membrane is thought to be a pulsating rather than a continuous flow. This is confirmed by the observation that the conductance to Na^+ of a planar membrane containing a small amount of gramicidin A fluctuates with time in a stepwise manner.[2]

Biological membranes are known to be highly selective permeability barriers, while artificial membranes are generally less selective for penetrants. These observations prompt us to consider the potential advantages of permselectivity in transport phenomena in the non-steady state. Several authors[3-5] have suggested advantages of operating various chemical processes in non-steady-state conditions. Paul[5] has shown that the selectivity for gas transport membrane processes was improved by increasing and decreasing the upstream pressure periodically in time with recovery of helium from natural gas being an example of where the pulsed membrane operation was useful.

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In the present study a poly(dimethyl siloxane) membrane was selected as a model membrane. Ratios of oxygen to nitrogen fluxes in the membrane are theoretically calculated for non-steady-state operation for the case when the upstream pressure is pulsed to keep the non-steady-state condition in effect continuously. Application of the concentration of uranium 235 utilizing a non-steady-state membrane separation method is also presented. The advantages of this method are considered and compared with the conventional steady-state process.

THEORY

Solutions of the diffusion equation have been summarized by several investigators.[6-9] However, it is useful to review the equation to make clear the results to be presented.

The diffusion of a penetrant in a planar membrane is governed by Fick's second law. If the initial and boundary conditions of concentration in the membrane are

$$C = C_1, \qquad x = 0, \qquad t \geq 0$$

$$C = C_2, \qquad x = L, \qquad t \geq 0$$

$$C = f(x), \qquad 0 < x < L \qquad t = 0 \tag{1}$$

the solution of the Fick's second law is

$$C(x) = C_1 + (C_2 - C_1)x/L - (2/\pi) \sum_{m=1}^{m'} \left(C_1(-1)^m - C_2\right)$$

$$\times \exp\left(-D_i(m\pi/L)^2 t\right)/m$$

$$+ (2/L) \sum_{m=1}^{m'} \exp\left(-D_i(m\pi/L)^2 t\right)$$

$$\times \sin(m\pi x/L) \int_0^L f(\xi)\sin(m\pi\xi/L) \, d\xi \tag{2}$$

where C is the concentration of the diffusing substance, x is the coordinate normal to the membrane, t is time, D_i is a constant diffusion coefficient of gas i, L is the membrane thickness and $f(x)$ is the initial concentration profile when $t = 0$. The flux of gas i at $x = L$, $J(i)$, is calculated from Fick's first law

$$J(i) = D_i(C_1 - C_2)/L$$

$$+ (2D_i/L) \sum_{m=1}^{m'} \left(C_1(-1)^m - C_2\right)\exp\left(-D_i(m\pi/L)^2 t\right)$$

$$- (2\pi D_i/L^2) \sum_{m=1}^{m'} m \exp\left(-D_i(m\pi/L)^2 t\right)(-1)^m \int_o^L f(\xi)\sin(m\pi\xi/L)d\xi$$

$$\tag{3}$$

The amount of gas i which has permeated through the membrane from $t = 0$ to $t = T$, $Q(i)$, is given by

$$Q(i) = D_i(C_1 - C_2)T/L$$

$$-(2L/\pi^2) \sum_{m=1}^{m'} \left((C_1(-1)^m - C_2)/m^2\right)\left(\exp\left(-D_i(m\pi/L)^2 T\right) - 1\right)$$

$$+(2/\pi) \sum_{m=1}^{m'} (-1)^m\left(\exp\left(-D_i(m\pi/L)^2 T\right) - 1\right)$$

$$\times \int_0^L f(\xi)\sin(m\pi\xi/L)\,d\xi/m \tag{4}$$

The upstream and downstream partial pressures of gas i, $p_1(i)$ and $p_2(i)$, are related to C_1 and C_2, assuming that Henry's law at the membrane surfaces by

$$C_1 = S_i p_1(i), \qquad C_2 = S_i p_2(i) \tag{5}$$

where S_i is the solubility coefficient of gas i.

RESULTS AND DISCUSSION

When $f(x) = 0$ and $C_2 = 0$, Eq. (4) reduces to Eq. (26) of ref. 7 which is commonly used to calculate the diffusion coefficient from the time-lag method. The calculations were performed for the permeation of oxygen and nitrogen in a poly(dimethyl siloxane) membrane using a FACOM M-180II AD (Fujitsu Ltd.) at the Meiji University Computer Center. In Eqs. (2)–(4), $m' = 1024$ was selected for the calculations in this study. Computational errors in the program developed in this study are found to be -6.776×10^{-21} for the flux calculations from Eq. (3).

Flux ratios for O_2 to N_2 in a poly(dimethyl siloxane) membrane are shown in Table I as a function of time. Sorption and transport parameters of the membranes[10] utilized in the calculations are summarized in Table II. It is seen

TABLE I
Flux and Flux Ratios of Oxygen and Nitrogen in a Poly(dimethyl Siloxane) Membrane[a]

t/L^2	$J(O_2)L/p_1(O_2)$	$J(N_2)L/p_1(N_2)$	$J(O_2)/J(N_2)$
600	9.925×10^{-17}	4.610×10^{-22}	215300
800	2.127×10^{-14}	1.902×10^{-18}	11800
1000	5.195×10^{-13}	2.739×10^{-16}	1897
1500	3.487×10^{-11}	1.958×10^{-13}	178.1
2000	2.738×10^{-10}	5.019×10^{-12}	54.55
5000	9.158×10^{-9}	1.412×10^{-9}	6.486
10000	2.431×10^{-8}	7.621×10^{-9}	3.189
50000	3.515×10^{-8}	1.800×10^{-8}	1.952
∞	3.515×10^{-8}	1.808×10^{-8}	1.944

[a]Unit: $J(i)L/p_1(i)/\text{cm}^2\text{s}^{-1}\text{cmHg}^{-1}$.

TABLE II
Diffusion and Solubility Coefficients of Oxygen and Nitrogen in a
Poly(dimethyl Siloxane) Membrane[a]

Gas	D_i	S_i
Oxygen	1.89×10^{-5}	1.86×10^{-3}
Nitrogen	1.23×10^{-5}	1.47×10^{-3}

[a]Units: $D_i/\text{cm}^2\text{s}^{-1}$; S_i/cmHg^{-1}.

in Table I that $J(O_2)/J(N_2)$ increases dramatically as the time decrease. $J(O_2)/J(N_2)$ at $t/L^2 = 600$ s/cm^2 is estimated to be 215,300, although the flux of O_2 is 10^{-9} times lower than that at steady state. It was reported[5] earlier that the selectivity for non-steady-state operation may be considerably higher than that at steady state for membrane separation processes. When oxygen and nitrogen are introduced to the upstream membrane surface at $t = 0$, the first molecules to reach the downstream surface must be oxygen due to its higher diffusivity over nitrogen. This idea indicates that $J(O_2)/J(N_2)$ should increase with a decrease of time as observed in the table.

Concentration profiles of oxygen and nitrogen in the membrane of $L = 0.01$ cm at $t = 0.01$ s, 0.15 s, and ∞ are shown in Figure 1. Concentration profiles of oxygen and nitrogen at $t = 0.01$ s and 0.15 s are found to decay to a negligible concentration with an increase of the distance, x, while concentration of both gases is allowed to be linear function of the distance at the steady state ($t = \infty$). It is observed in the figure that oxygen penetrates faster than nitrogen in the membrane at the time before reaching the steady state. This observation is directly related to the high flux ratios of oxygen to nitrogen in Table I.

It becomes evident from the above that the selectivity of permeation under the non-steady-state conditions can be much higher than at the steady state,
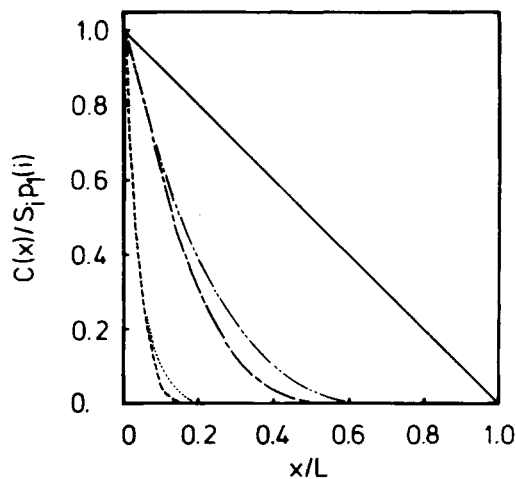

Fig. 1. Concentration profiles of oxygen and nitrogen in the membrane of $L = 0.01$ cm. ($\cdots$): $t = 0.01$ s, O_2, ------: $t = 0.01$ s, N_2, —---—: $t = 0.15$ s, O_2, —·—: $t = 0.15$ s, N_2, ——: $t = \infty$, O_2 or N_2.

although non-steady-state flux is much less than that at the steady state. The permeation time needed for such non-steady-state operation is generally too short to be utilized practically for conventional permeation conditions. For the present model membrane with $L = 0.01$ cm, the time over which non-steady-state operation shows these advantages is only 2 or 3 s. One solution may be to force a continuous non-steady-state permeation condition by having the upstream pressure pulsate as suggested by Paul.[5] The calculations are performed hereafter under the conditions that the upstream pressure is varied with a period of $T_1 + T_2$. The conditions are expressed as Eq. (6).

$$p_1(i) = p_1'(i) \qquad \text{at } (T_1 + T_2)n \le t < T_1 + (T_1 + T_2)n$$

$$p_1(i) = p''_1(i) \qquad \text{at } T_1 + (T_1 + T_2)n \le t < (T_1 + T_2)(n + 1) \quad (6)$$

Where n stands for a plus integer.

The calculations of $J(i)$ and $Q(i)$ at time t' can be done step by step during each interval when the upstream pressure is constant and the following equations are obtained.

If $(T_1 + T_2)n \le t' < T_1 + (T_1 + T_2)n$

$$J(i) = \sum_{h=0}^{n} \left(J_i(T_1, h) + J_i(T_2, h) \right) + J_i\left(t' - (T_1 + T_2)n, n \right)$$

$$Q(i) = \sum_{h=0}^{n} \left(Q_i(T_1, h) + Q_i(T_2, h) \right) + Q_i\left(t' - (T_1 + T_2)n, n \right) \quad (7)$$

If $T_1 + (T_1 + T_2)n \le t' < (T_1 + T_2)(n + 1)$

$$J(i) = \sum_{h=0}^{n} \left(J_i(T_1, h) + J_i(T_2, h) \right) + J_i(T_1, n)$$

$$+ J_i\left(t' - (T_1 + T_2)n - T_1, n \right)$$

$$Q(i) = \sum_{h=0}^{n} \left(Q_i(T_1, h) + Q_i(T_2, h) \right) + Q_i(T_1, n)$$

$$+ Q_i\left(t' - (T_1 + T_2)n - T_1, n \right) \quad (8)$$

Where $J_i(T_1, h)$ is the flux of gas i calculated by Eq. (3) on the conditions of $t = T_1$ and $p_1(i) = p_1'(i)$, and $f(x)$ is $C(x)$ at $t = (T_1 + T_2)h$. $J_i(T_2, h)$ is the flux on the conditions of $t = T_2$, $p_1(i) = p_1''(i)$ and $f(x) = C(x)$ at $t = (T_1 + T_2)h + T_1$ where $f(x) = 0$ when $h = 0$. $J_i(t' - (T_1 + T_2)n, n)$ and $J_i(t' - (T_1 + T_2)n - T_1, n)$ are the fluxes on the conditions of $t = t' - (T_1 + T_2)n$, $p_1(i) = p_1'(i)$ and $f(x) = C(x)$ at $t = (T_1 + T_2)n$ and the conditions of $t = t' - (T_1 + T_2)n - T_1$, $p_1(i) = 0$ and $f(x) = C(x)$ at $t = (T_1 + T_2)n + T_1$. $Q_i(T_1, h)$ is the permeated amount of gas i calculated by Eq. (4) on the conditions of $T = T_1$, $p_1(i) = p_1'(i)$ and $f(x) = C(x)$ at $t = (T_1 + T_2)h$ and $Q(T_2, h)$ is the amount permeated at the conditions of $T = T_2$, $p_1(i) = p_1''(i)$ and $f(x) = C(x)$ at $t = (T_1 + T_2)h + T_1$. $Q_i(t' -$

$(T_1 + T_2)n, n)$ and $Q_i(t' - (T_1 + T_2)n - T_1, n)$ are the amounts permeated at the conditions of $T = t' - (T_1 + T_2)n$, $p_1(i) = p_1'(i)$ and $f(x) = C(x)$ at $t = (T_1 + T_2)n$ and the conditions of $T = t' - (T_1 + T_2)n - T_1$, $p_1(i) = p_1''(i)$ and $f(x) = C(x)$ at $t = (T_1 + T_2)n + T_1$. The flux and the amount permeated at the non-steady state can be calculated from the extension of Eqs. (3) and (4) considering the initial concentration profiles when the upstream pressure is pulsating with a period of $T_1 + T_2$.

Figure 2 shows $J(i)/p_1'(i)$ for oxygen and nitrogen as a function of the time for the conditions: $T_1 = 0.15$ s, $T_2 = \infty$, $L = 0.01$ cm, and $p_1''(i) = 0$. These conditions correspond to the gases being introduced to the upstream side only once during $0 \leq t \leq 0.15$ s and then evacuated at $t > 0.15$ s (Case I). When the fluxes for Case I are compared to those calculated at $T_1 = \infty$ (Case II), it is found that the Case I fluxes of oxygen and nitrogen agree within 2% with those for Case II until $t = 0.3$ s for oxygen and 0.40 s for nitrogen. These results indicate that the amounts until $t = 0.3$ s for oxygen and 0.4 s for nitrogen are mainly those which already penetrated into the upstream surface of the membrane until $t = 0.15$ s. The maximum fluxes of oxygen and nitrogen are produced at $t = 0.57$ s for oxygen and $t = 0.83$ s for nitrogen. It is also observed that the flux of oxygen increases with time until $t = 0.57$ s and is higher than that of nitrogen until $t = 1.77$ s. The flux of oxygen is, on the contrary, decreases faster than that of nitrogen at $t > 1.77$ s. This is due to the higher diffusivity of oxygen than that of nitrogen. Oxygen tends to sweep away faster than nitrogen, and therefore, the flux of nitrogen is higher than that of oxygen at $t > 1.77$ s.

Figure 3 shows $J(O_2)/J(N_2)$ for the conditions of $T_1 = 0.15$ s, $T_2 = 15$ s, $L = 0.01$ cm and $p_1''(i) = 0$ as a function of time. $J(O_2)/J(N_2)$ exhibits periodic changes during the period $T_1 + T_2$ and gives values higher or lower than unity depending on the time. The most striking aspect of these results is
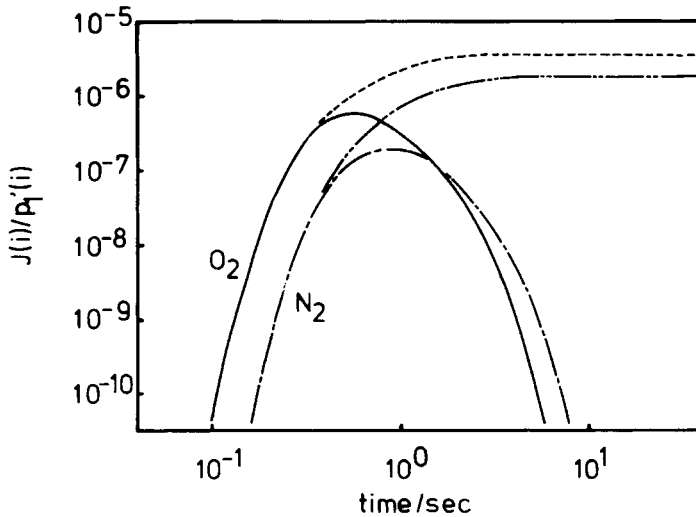

Fig. 2. $J(i)/p_1'(i)$ of oxygen (——) and nitrogen (—·—) on the conditions of $T_1 = 0.15$ s, $T_2 = \infty$, $L = 0.01$ cm, and $p_1''(i) = 0$, and of oxygen (-----) and nitrogen (———) on the conditions of $T_1 = \infty$ and $L = 0.01$ cm as a function of time.
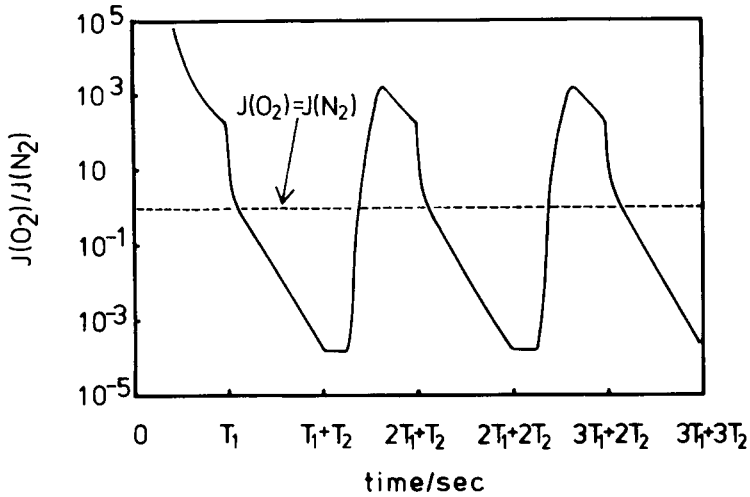
Fig. 3.   Flux ratios of oxygen to nitrogen vs. time.

that the poly(dimethyl siloxane) behaves like a nitrogen-selective membrane at $(T_1 + T_2)n + T_1 < t < (T_1 + T_2)(n + 1) + 2T_1/5$ and a similar tendency is found in Figure 2 at $t > 1.77$ s. The membrane shows preferential oxygen selectivity at $(T_1 + T_2)n + 2T_1/5 < t < (T_1 + T_2)(n + 1)$ as normally observed for conventional nonporous membranes.

Figure 4 shows $J(i)/p_1'(i)(i = O_2$ or N_2) on the conditions of $T_1 = 0.15$ s, $T_2 = 15$ s, $L = 0.01$ cm, and $p_1''(i) = 0$ as a function of time. fluxes of both gases increase with time at $(T_1 + T_2)n < t < (T_1 + T_2)n + T_1$, while those for both gases decrease with time at $(T_1 + T_2)n + T_1 < t < (T_1 + T_2)(n + 1)$. When both gases are introduced to the upstreamside and the upstream
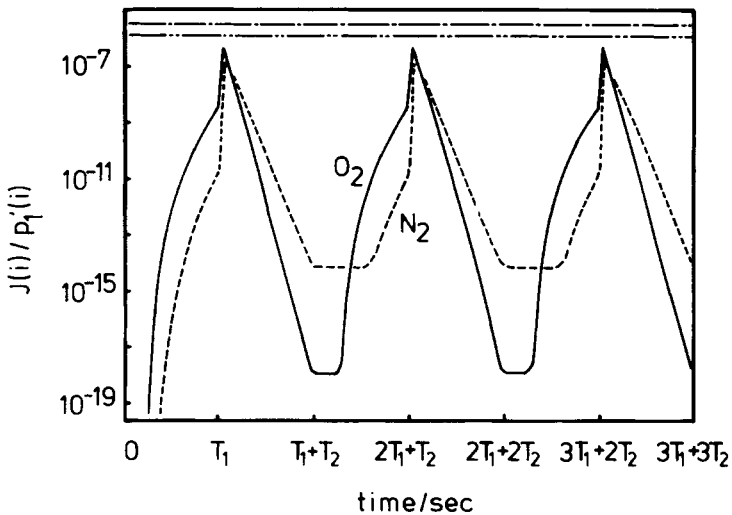

Fig. 4. $J(i)/p_1'(i)$ of oxygen (——) and nitrogen (-----) on the conditions of $T_1 = 0.15$ s, $T_2 = 15$ s, $L = 0.01$ cm, and $p_1''(i) = 0$, and of oxygen (—·—) and nitrogen (—---—) at the steady state.

TABLE III
Permeated Amount of Oxygen to Nitrogen on the Conditions of $T_1 = 0.15$ s and $T_2 = 0.15 \sim \infty$[a]

T_1	T_2	$Q_{O_2}(T_1, \infty)/Q_{N_2}(T_1, \infty)$	$Q_{O_2}(T_2, \infty)/Q_{N_2}(T_2, \infty)$
0.15	0.15	1.973	1.932
0.15	1.5	0.9390	2.004
0.15	3.0	0.4011	1.957
0.15	6.0	0.9693	1.945
0.15	9.0	30.91	1.944
0.15	12.0	218.1	1.944
0.15	15.0	259.9	1.944
0.15	100.0	261.3	1.944
0.15	∞	265.2	1.944

[a]Units: T_1/s; T_2/s.

pressure is kept constant at $p_1'(i)$, oxygen diffuses faster than nitrogen in the membrane and the flux of oxygen, therefore, increases faster than that of nitrogen with time at $(T_1 + T_2)n < t < (T_1 + T_2)n + T_1$. At $(T_1 + T_2)n + T_1 < t < (T_1 + T_2)(n + 1)$ when gases are evacuated and the upstream pressure is zero, oxygen diffuses out of the membrane faster than nitrogen, and the concentration of oxygen in the membrane is less than that of nitrogen. This indicates that the flux of nitrogen becomes greater than that of oxygen with a certain period as is observed in Figures 2 and 3.

The ratios of permeated amounts of oxygen and nitrogen, $Q_{O_2}(T_1, \infty)/Q_{N_2}(T_1, \infty)$ and $Q_{O_2}(T_2, \infty)/Q_{N_2}(T_2, \infty)$ are summarized in Table III and the dependence of $Q_i(T_1, \infty)$ and $Q_i(T_2, \infty)$ on T_2/T_1 are shown in Figure 5 where $Q_i(T_1, \infty) = \int_{(T_1 + T_2)n}^{(T_1 + T_2)n + T_1} J(i)\, dt$, $Q_i(T_2, \infty) = \int_{(T_1 + T_2)n + T_1}^{(T_1 + T_2)(n + 1)} J(i)\, dt$, $i = O_2$ or N_2 and $T_1 = 0.15$ s. Table III and Figure 5 are values for the condition of
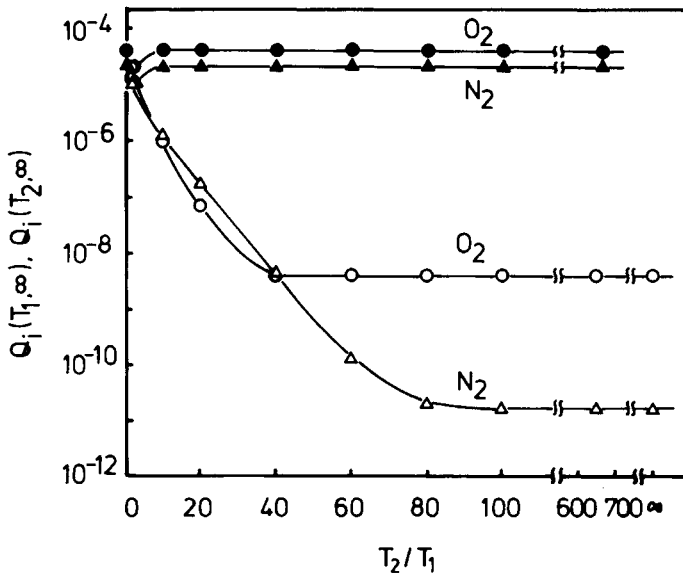

Fig. 5. Plots of $Q_{O_2}(T_1, \infty)$ (open circles), $Q_{N_2}(T_1, \infty)$ (open triangles), $Q_{O_2}(T_2, \infty)$ (closed circles), and $Q_{N_2}(T_2, \infty)$ (closed triangles) vs. T_2/T_1.

$(T_1 + T_2)n \geq 10$, since it is found that $Q_i(T_1, n)$ or $Q_i(T_2, n)$ does not depend on n within the computational error on the condition of $(T_1 + T_2)n \geq 10$. It is found in Figure 5 that $Q_i(T_1, \infty)$ does not depend on T_2, while $Q_i(T_2, \infty)$ decreases with the increase of T_2 until a certain time. In Table III $Q_{O_2}(T_1, \infty)/Q_{N_2}(T_1, \infty)$ on the conditions of $T_2 \geq 12.0$ s, $T_1 = 0.15$ s, and $n > 0$ is calculated to be nearly equal to that on the conditions of $T_2 = \infty$ and $T_1 = 0.15$ s, while $Q_{O_2}(T_1, \infty)/Q_{N_2}(T_1, \infty)$ decreases with the decrease of T_2 on the conditions of $T_2 < 12.0$ s and $T_1 = 0.15$ s. The low selectivity of $Q_i(T_1, \infty)$ between oxygen and nitrogen at $T_2 < 12.0$ s should be due to the fact that the time interval T_2 is not long enough to evacuate gases from inside the membrane and that the initial concentration profiles at $t = (T_1 + T_2)n$ are unable to become essentially zero within this time interval.

$Q_{O_2}(T_1, \infty) + Q_{O_2}(T_2, \infty)$ and $Q_{N_2}(T_1, \infty) + Q_{N_2}(T_2, \infty)$ at the values of any T_1 and T_2 should be in fair agreement with $T_1 \cdot J(O_2)$ and $T_2 \cdot (N_2)$ at the steady state, because all gases that enter the membrane must go out from the membrane. $Q_{O_2}(T_2, \infty)/Q_{N_2}(T_2, \infty)$ should, therefore, remain close to the values of the relatively low selectivity due to the high permeated amount of $Q_i(T_2, \infty)$ compared to $Q_i(T_1, \infty)$ as is shown in Figure 5.

Another attractive application of the present notion is also examined in this study. The separation of the isotope compounds is generally known to be difficult due to their similar chemical and physical properties. The ideal separation factor for the concentration of uranium 235 by a membrane process is reported to be 1.004299,[11] which is the square root of molecular weight of uranium 238 hexafluoride divided by that of uranium 235 hexafluoride. The present notion is extended to the concentration of the uranium 235 from natural uranium. The model calculations are performed on the conditions of $D(^{235}U) = 1.00429 \times 10^{-5}$ cm^2/s, $D(^{238}U) = 1.00000 \times 10^{-5}$ cm^2/s, $S(^{235}U) = S(^{238}U) = 1$, and $p_2(i) = 0$. Reduced fluxes for uranium 235 and uranium 238 and the ratios of the fluxes calculated from Eq. (3) are summarized in Table IV. $J(^{235}U)/J(^{238}U)$ at $t/L^2 = 800$ is estimated to be 1.144.

It is known that for the process to have 5% concentration of uranium 235, it should be repeated 900 times at the steady state.[11] If the uranium concentration is performed by non-steady-state membrane methods and the flux ratio of the uranium 235 to the uranium 238 is selected to be 1.144 as the model calculation, the repeated number of the penetration of the uranium gases to

TABLE IV
Fluxes of Uranium 235 and 238

t/L^2	t	$J(^{235}U)L/p_1(^{235}U)$	$J(^{238}U)L/p_1(^{238}U)$	$J(^{235}U)/J(^{238}U)$
800	0.08	3.880×10^{-18}	3.391×10^{-18}	1.144
900	0.09	1.159×10^{-16}	1.027×10^{-16}	1.129
1000	0.10	1.747×10^{-15}	1.567×10^{-15}	1.115
1500	0.15	5.728×10^{-12}	5.324×10^{-12}	1.076
2000	0.20	3.143×10^{-10}	2.974×10^{-10}	1.057
5000	0.50	3.482×10^{-7}	3.400×10^{-7}	1.024
10000	1.00	2.967×10^{-6}	2.928×10^{-6}	1.013
∞	∞	1.004×10^{-5}	1.000×10^{-5}	1.004

[a]Units: t/L^2/cm^{-2}s; t/s; $J(i)L/p_1(i)$/cm^{2}s^{-1}cmHg^{-1}.

the membrane is only required 29 times in this case because 1.144^{29} is nearly equal to $1.00429.^{900}$ This result indicates that the membrane device for the concentration of the uranium 235 will become the size of $1/31$ $(= 29/900)$ compared to the conventional device and will lead to the curtailment of operating costs if the upstream pressure is regulated and the permeation occurs at the non-steady state.

One of the focuses of the recent investigation of membrane sciences is how to make thin active layers of the membranes that lead to high flux membranes. In the investigation of Langmuir Blodgett, asymmetric and plasma coating membranes are examples. On the contrary, thick membrane will be required to use the present idea, since a practical time interval of the upstream pressure pulse can be achieved only under these conditions. The disadvantage of the non-steady-state separation method is that the fluxes are much smaller than those at steady state and that the flux ratios depend on time. It is, therefore, necessary to collect the enriched penetrants for a certain fraction of the interval using fraction collectors. The method seems, however, to be an attractive idea, since there are possibilities that isotope concentration can be performed more economically and on a smaller scale.

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