Single Gas Permeation through Porous Glass Modified with Tetraethoxysilane

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Porous glass is a widely-used inorganic porous membrane material, characterized by its small pore size and sharp distribution. Therefore, it has been the subject of much research since the 1950s. In recent years, inorganic membranes have drawn growing attention, and their application studies have been carried out using porous glass as a typical inorganic membrane. The advantages of inorganic membranes in thermal and chemical stabilities over organic membranes have been verified through research, while some disadvantages have also been pointed out, such as their poor selectivity and difficulty in thinning. At this stage, however, only limited research is available regarding the improved selectivity of inorganic membranes. Schnabel and Vaulont (1978) improved the desalination property of porous glass membrane by surface modification. The authors (1987, 1988) modified the surface condition of a porous glass membrane to control the surface transport property and reported the possibility of improving the gas selectivity.

It is agreed generally that a membrane with uniform pores on the order of angstroms and the level of molecular size would have excellent selectivity. For a long time, the order of the uniform pore size of inorganic membranes had been limited to the order of a few tens of angstroms for porous glass, where the selectivity by gas-phase flow only had an upper limit predicted by Knudsen's equation.

Recently, some experimental research into fine pore control was reported. Niwa et al. (1984) presented a method in which tetraethoxysilane (TEOS) was adsorbed on zeolite powders having pores smaller than the TEOS molecule and decomposed. The method did not change the acidity, but did reduce the size of pore opening. Asaeda and Du (1986) formed a thin film of alumina on porous support by the sol-gel method controlling the pore size by hydrothermal reaction. This membrane showed high selectivity for water-alcohol mixture. Koresh and Sofer (1983) made carbon membranes with fine pores by controlling oxidation condition.

In the previous paper (Okubo and Inoue, 1989), the authors proposed a new approach of controlling fine pores, in which tetraethoxysilane was introduced into pores and decomposed on the pore wall, and reported an improvement in helium–oxygen selectivity through porous glass membrane. In this paper, results of single-gas permeation experiments with seven gases at 323–473 K are presented, and the mechanism of permeation through the modified porous glass is estimated.

Single Gas Permeation

Single-gas permeation experiments using seven gases—helium, oxygen, nitrogen, carbon dioxide, argon, hydrogen, and neon—were carried out at 323–473 K through the porous glass modified with the same method as in the previous paper (Okubo and Inoue, 1989). Arrhenius plots of permeation rates through both the original and the modified porous glasses are shown in Figure 1. The accuracy of the measurement was within 3% at most. The permeation rates of helium, argon, hydrogen and neon through the modified glass increased with temperature. The apparent activation energies are summarized in Table 1.

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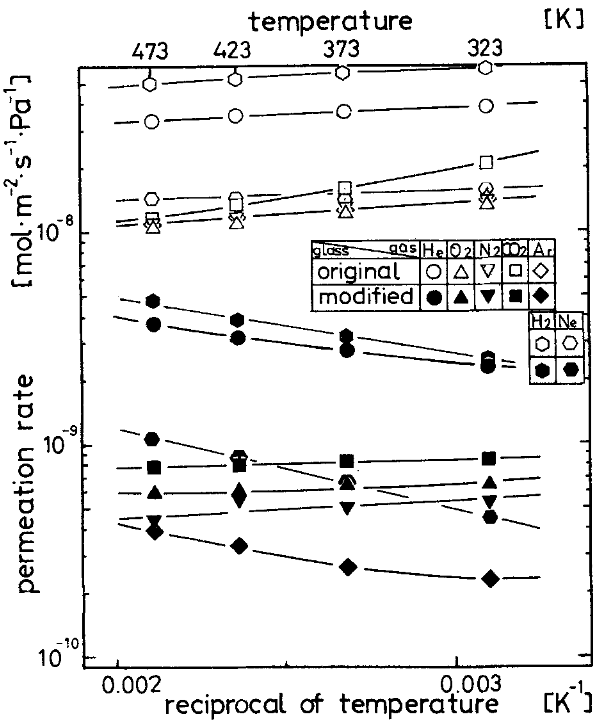

Figure 1. Arrhenius plots of permeation rates.

Each permeation rate through the modified glass was smaller than that through the original glass, but the reversed rates for nitrogen and oxygen and the decrease in that for argon after modification were noteworthy.

The ratios between permeation rate through the modified glass and that through the original glass changed with different temperature, as shown in Figure 2. The values increased as temperature increased, varying markedly with gas species. This result indicated that the selectivity was introduced successfully to the porous glass membrane not only for the helium-oxygen mixture but also for other gas species.

On the basis of the modified glass structure shown in the previous paper (Okubo and Inoue, 1989), the permeation resistances of a pore of 2-nm radius and the active part formed by the decomposition were expected to be connected in series. As the decrease in porosity by modification was on the order of a few percent, permeation rates through the active part were estimated by Eq. 1.

$$1/R_{\mathrm{mod}} = 1/R_{\mathrm{org}} + 1/R_{\mathrm{act}} \tag{1}$$

The differences between the permeation rates through the modified glass and the estimated values were small enough, on the order of a few percent. This estimation proved that the permeation rates through the modified glass corresponded to those through the active part.

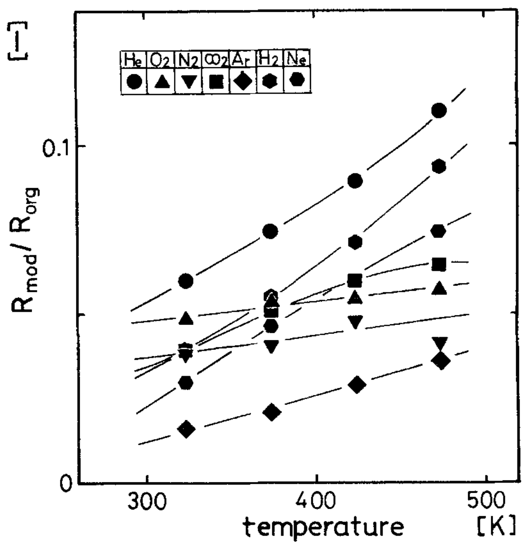

Figure 2. Changes in $R_{\mathrm{mod}}/R_{\mathrm{org}}$ with temperature.

Table 1. Apparent Activation Energy for Permeation

Gases	kJ · mol^{-1}
Helium	3.9
Argon	4.6
Hydrogen	5.3
Neon	7.1

Discussion

In the Knudsen regime where the collision of a molecule with a wall is dominant in gas diffusion, the corrected permeability $Q(MT)^{1/2}$, the product of the permeability and the square root of molecular weight and temperature, is independent of gas spe-

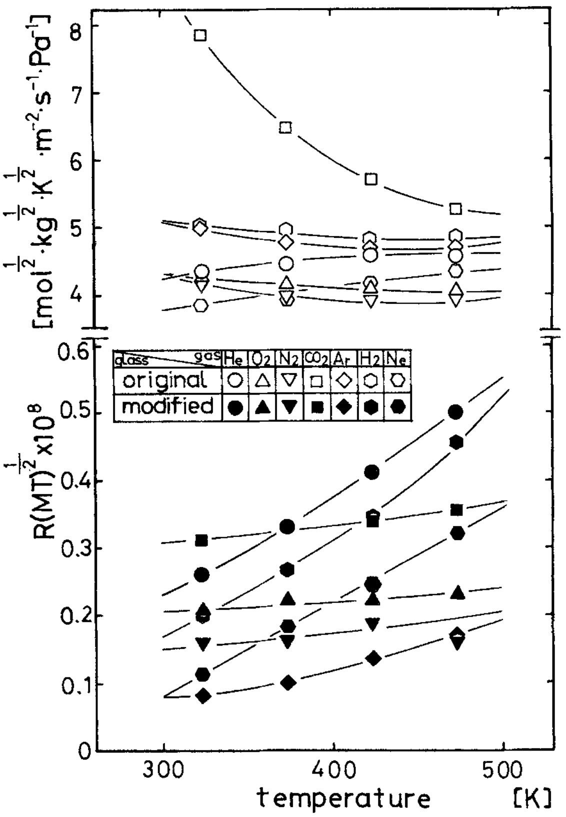

Figure 3. Changes in $R(MT)^{1/2}$ with temperature.

cies or temperature and dependent only on the pore structure without the contribution of surface or condensed flow.

$$Q\sqrt{MT} = \frac{\epsilon}{k^2}\frac{4}{3}\frac{2-f}{f}r\sqrt{\frac{2}{\pi R_g}} \tag{2}$$

As the modified glass in the present work was asymmetrical, the degree of permeation is evaluated as the permeation rate, the ratio of permeability and membrane thickness. Corrected permeation rates through the original and the modified porous glasses are shown in Figure 3. The tendency for the original porous glass was similar to those presented by Hwang and Kammermeyer (1966) and Shindo et al., (1983). On the other hand, the corrected permeation rates through the modified glass (that is, through the active part) increased greatly with temperature, especially those of helium, argon, hydrogen and neon. This tendency was quite different from that for the original glass.

On the basis of the results mentioned above, the permeation mechanism can be estimated. As shown in Figures 1 and 3, it can be reasonably concluded that the mechanism for the original glass consisted of Knudsen flow and surface flow; it was also pointed out by previous researchers. Pore control or enclosure, however, can be expected after modification. As the pore becomes smaller, the permeation mechanism would change from Knudsen regime to micropore diffusion (molecular sieve) regime. Moreover if the pore is enclosed, a gas molecule dissolves in and diffuses through the membrane. Potential profiles across the pore are illustrated in Figure 4. Since condensed flow is not expected of the gas species used in this paper, on the basis of Kelvin's equation, mechanisms expected are limited to those shown in Figure 4 and solution-diffusion.

The case of Knudsen flow with surface flow is considered first. The corrected permeation rates through the modified glass did not show a unified value by gas species; and those of helium, argon, hydrogen and neon increased greatly with temperature. The contribution of the surface flow could account for the increase in the low-temperature region, but could not account for the tendency for the modified glass shown in Figure 3. The

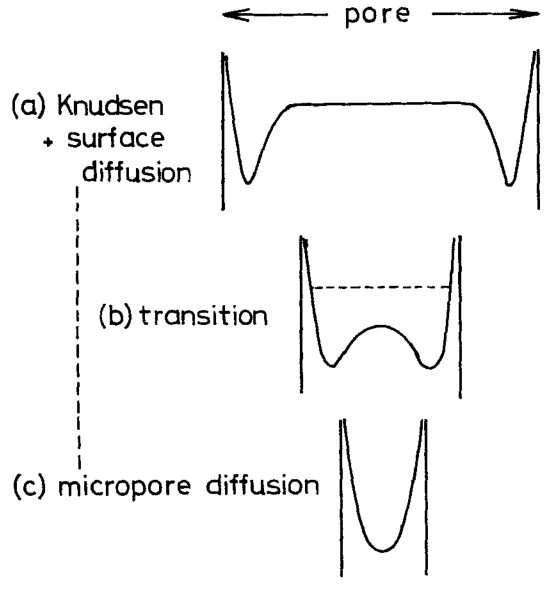

Figure 4. Potential profiles in a pore.

Table 2. Specific Energies on 4A Zeolite

Gases		kJ · mol^{-1}		
		E_a	Q_{iso}	$E_a - Q_{iso}$
Argon	E&A*	20	12	7.5
	R&D**	24	14	10
Nitrogen	E&A*	35	26	8.8
	R&D**	25	18	7.3

*Determined by Eagan and Anderson (1975)
**Determined by Ruthven and Derrah (1975)

Knudsen diffusivity was derived as follows (Knudsen, 1909; Smoluchowski, 1910):

$$D_k = \frac{4}{3}\frac{2-f}{f}r\sqrt{\frac{2R_gT}{\pi M}} \tag{3}$$

where f represents the fraction of the molecules to reflect diffusively. Many experimental results since Wood (1915) generally assume f to be unity. The development of the molecular-beam technique, however, provided several examples in which f was smaller than unity (Hurlbut, 1957; Asada, 1981). As the pore is smaller, the potential well is expected to be shallower, as shown in Figure 4. Therefore, a molecule at higher temperature (that is, one with larger kinetic energy) might reflect less diffusively since attainment of thermal equilibrium between a molecule and a wall would be harder. Based on this theoretical consideration, it was decided that the change of f might be proper. Still, there is no experimental proof to support the change of f in porous materials, and the f value must change greatly (for example, 0.5–1) to account for the experimental results shown in Figure 1. Consequently, it is hard to conclude at present that a change of f is a dominant factor. The discussion above removes the possibility that Knudsen flow with surface flow is the mechanism.

The cases of micropore diffusion mechanism and solution-diffusion mechanism are considered next. If permeation is described in terms of activated process, both mechanisms can be treated similarly. In this study experiments were carried out in higher temperature and the pore size of the active part was monodisperse type. Therefore, adsorption or dissolution equilibrium is expressed as the Henry type, and the apparent activation energy for permeation is equal to the activation energy for diffusion minus the specific heat of adsorption or dissolution. In sur-

Table 3. Apparent Activation Energy for Helium Permeation through Nonporous Glass

Glass Code No.	Apparent Activ. Energy kJ · mol^{-1}
7900 (Vycor)	21* 20**
Fused silica	21* 20**
7740	27* 27**
0080	46* 46**

*By Norton (1953)
**Altemose (1961)

face diffusion, the activation energy must be smaller than the specific heat of adsorption because of the coexistence of the gas-phase flow, but opposite cases are possible in micropore diffusion or solution-diffusion.

For micropore diffusion in 4A zeolite, typical values by Ruthven and Derrah (1975), and Eagan and Anderson (1975) are summarized in Table 2. The differences are a little larger than the apparent activation energies in Table 1.

For solution-diffusion, typical apparent activation energies by Norton (1953) and Altemose (1961) are shown in Table 3. These are values for helium through silicate glasses, but are much larger than those in Table 1. Therefore, it is hard to adopt the solution-diffusion mechanism through enclosed pores. And the solution-diffusion mechanism could not account for the result that the permeation rates did not decrease to zero in the modification (Okubo and Inoue, 1989), for the enclosed part would be thicker and the permeation rates would decrease monotonously to zero in the presence of TEOS.

Consequently, the permeation mechanism was estimated to be diffusion through the pores small enough to deviate from Knudsen's equation. That is, the wall effect is thought to prevail all over the permeating molecules in pores. This mechanism could be called the transition regime in Figure 4. The finding that permeation rates do not decrease to zero indicates that the pore was so small that a TEOS molecule could not diffuse and decompose. In other words, the size of TEOS molecule could determine the final pore size.

Notation

D_k = Knudsen diffusivity, m^2 · s^{-1}
f = reflection coefficient
k^2 = tortuosity factor
M = molecular weight, kg · mol^{-1}
Q_k = Knudsen permeability, mol · s^{-1}· m^{-1} · Pa^{-1}
r = pore radius, m
R = permeation rate, mol · s^{-1} · m^{-2} · Pa^{-1}
R_g = gas constant, J · K^{-1} · mol^{-1}
T = temperature, K

Subscript

act = active part
mod = modified porous glass
org = original porous glass

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