

# Mixed Gases Separation by Fine Porous Freeze-Dried Cellulose Acetate Membrane

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## Synopsis

A freeze-dried cellulose acetate membrane with high permeability and high separation factor was prepared. In the successive membrane process, the heat treatment temperature was 80°C for constant period of 10 min, acetone evaporation time was between 4 and 6 min, and the membrane was fixed during drying to prevent shrinkage. Gas permeabilities for such a membrane were inversely proportional to the square root of molecular weight, suggesting that the mechanism of gas flow through this membrane was Knudsen flow. Separation factors for H<sub>2</sub>-He, Ar-Kr, N<sub>2</sub>-Kr, He-Ne, H<sub>2</sub>-Ne, He-Ar, Ar-H<sub>2</sub>, He-Kr, Ar-He, and He-H<sub>2</sub> were measured. These factors were higher than those of membranes reported already. Separation efficiency largely depended upon the combinations of mixed gases. The combination of two atom molecules and one atom molecule lowered the separation efficiency compared with the combination of one atom molecule and one atom molecule.

## INTRODUCTION

Gas separation by permeation through membranes has been suggested for many years.<sup>1,2</sup> Gas separation membrane may be divided into two categories, i.e., homogeneous dense and porous.<sup>3</sup> In homogeneous dense membrane, gas molecules permeate through a membrane by a solution-diffusion mechanism.<sup>4</sup> The solubility difference between gases to the membrane is the most important factor for mixed gases separation. On the other hand, for the porous membranes, mixed gases are separated by the gas molecular weights differences,<sup>5</sup> which is suitable for the separation of isotopes, rare gases, and gases which have few differences between solubilities. The separation factor for gases by porous membrane is given by the relation between pore diameter ( $d$ ) and mean free path ( $\lambda$ ) for a gas.<sup>6</sup> When the pore is large enough ( $d \gg \lambda$ ), the viscous flow does not separate gases. On the contrary, when the pore is very small ( $d \ll \lambda$ ), compared with the mean free path, Knudsen flow does separate gases. These indicate that all porous membranes have separability of mixed gases by controlling the relation between mean free path and pore diameter. Nevertheless, the small pore size membrane is requested, because it is used in the high pressure state being short mean free path. The gas flux through porous membrane is expressed by

$$J = K(\Delta p/L) \quad (1)$$

$$K = (\epsilon/q^2)K^* \quad (2)$$

where  $K$  is a permeability,  $\Delta p$  is a pressure difference between high and low pressure side,  $L$  is thickness,  $\epsilon$  is porosity,  $q$  is tortuosity factor, and  $K^*$  is a hole

permeability, which is a function of pore radius. It is very difficult to get a high flux with small pore size. Because  $\epsilon$  and  $K^*$  decrease when the pore size decreases. However, small tortuosity factor and thin thickness membrane may have a high flux from eqs. (1) and (2) without increasing pore diameter. It has been suggested that freeze-dried cellulose acetate membrane for hyperfiltration has a possibility of obtaining high flux and separation at the same time.<sup>7</sup> Such a membrane is composed of a thin skin layer and a thick large porous matrix layer as a supporting substance. The permeation and separation properties are mainly determined by the skin layer, which is considered to be a homogeneous dense structure. Dried cellulose acetate is in the glassy state at room temperature. It is supposed that such a glassy polymer includes a large amount of small voids.<sup>8</sup> If this voids traverse through skin layer, it may be used as a fine porous asymmetric membrane for gas separation. Membrane structure is determined during membrane preparation process. We tried to find a good condition for such a membrane. Lastly, permeation and separation factor for H<sub>2</sub>, He, Ne, N<sub>2</sub>, Ar, and Kr gases were measured.

## EXPERIMENTAL

### The Membrane Preparation Process

The membrane preparation process is shown sequentially in Figure 1.<sup>7</sup> The mixed solution of formamide, acetone and cellulose acetate (Eastman Chemical Co., Ltd., E398-3) was cast on a flat glass plate. The mixing percentage of each substance was 30%, 45%, and 25% in weight, respectively. The cast solution was left on the glass plate for several minutes. This time was called as acetone evaporation time. After that it was immersed in cold water (4°C), and the solvent was exchanged with water. The swollen membrane was annealed in hot water for 10 min to obtain a dense skin layer. The annealed membrane was frozen at -80°C in isopentane for 30 s, and successively freeze-dried at -23°C in desiccator connected to a vacuum pump for 24 h and dried at +15°C for 12 h.

In Figure 2 the tensile force change, which was measured uniaxially, was plotted as a function of freeze-drying time. Such a tension was given by the membrane shrinkage with water evaporation. The swollen membrane was fixed on the frame during drying time in order to prevent a shrinkage, which might represent the same effect as stretching the membrane biaxially. The membranes, which had acetone evaporation times longer than 3 min, indicated characteristic remarks, as shown in Figure 2. They shrunk to become transparent and dense, if they were not fixed on the frame. The prepared membrane was opaque, implying a porous structure. The membrane thickness was about 150  $\mu\text{m}$ .

### Permeability and Separation Factor Measurements

Figure 3 shows an outline of apparatus for permeability and separation factor measurements, which are a little improved in comparison with the measurements reported by Agrawal and Sourirajan.<sup>7</sup> Permeability measurements are made in accordance with the following experimental procedures. Gases are fed into the high pressure side. The gases flow rate through the membrane at the low

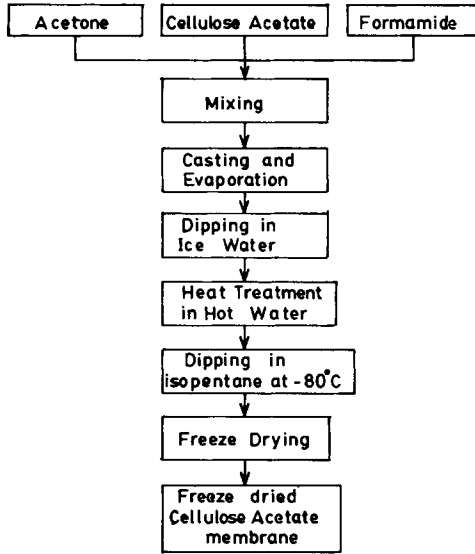


Fig. 1. Membrane process flow chart.

pressure side can be generally expressed by

$$J = -K(p_B - p_F)/L \tag{3}$$

where  $K$  is a permeability constant,  $p_F$  is pressure on the high pressure side. In this experiment  $p_B$  was always 1 atm.

Separation factor measurement is carried out by following experimental procedures. The mixed gases, in which the molar fraction of a based gas is 99.5%

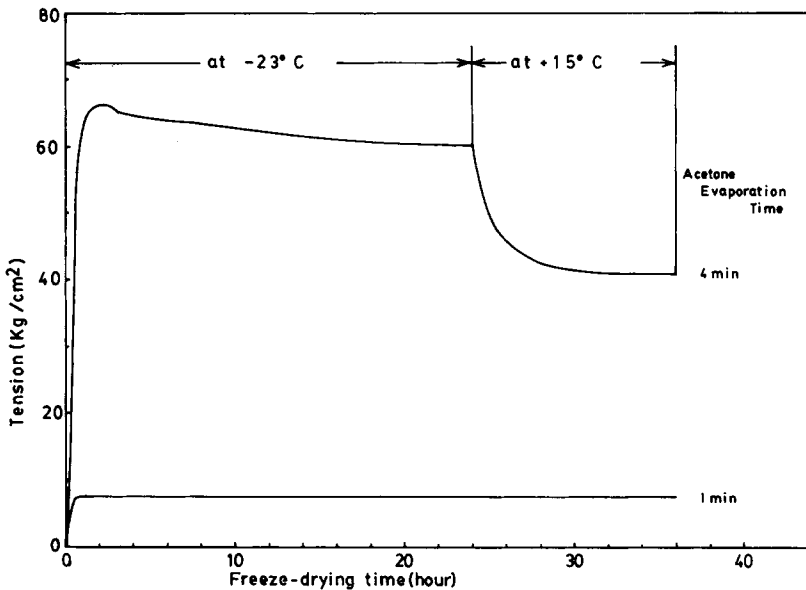


Fig. 2. Tensile force change in freeze drying of cellulose acetate membrane as a function of time.

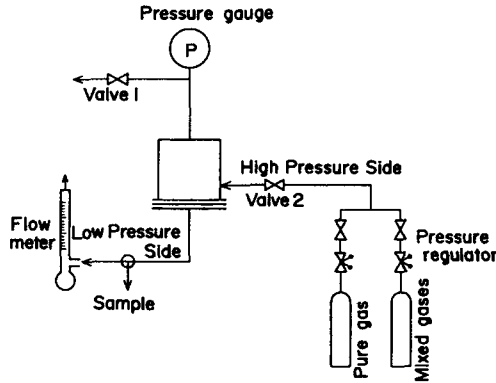


Fig. 3. Gas permeability testing apparatus.

and that of the gas marked to be separated is 0.05%, are supplied into the high pressure side. The mixed gas on this side is leaked from valve 1 to maintain a constant molar fraction. The pressure on the high pressure side is always constant. The permeated mixed gas compositions were measured by gas chromatography after sampling with a syringe. The pressure on the low pressure side always stays at 1 atm. Temperature during measurements was 25°C. The separation factor is defined as

$$\alpha = (x_B/1 - x_B)/(x_F/1 - x_F) \quad (4)$$

where  $x_B$  and  $x_F$  are molar fractions of marked light gas in the low pressure side and the high pressure side, respectively. If the Knudsen flow is predominant in the porous media, the separation factor takes an ideal value, which becomes the square root ratio of molecular weight for gas molecules,

$$\alpha_0 = (M_2/M_1)^{1/2} \quad (5)$$

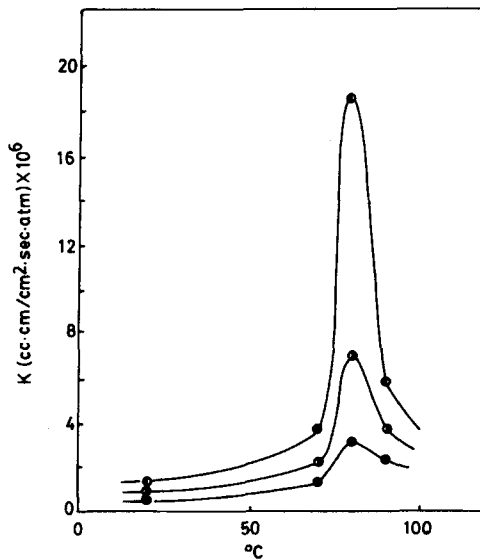


Fig. 4. Heat treatment temperature effect on gas permeabilities: (○) Ar; (○) Kr; (●) Xe.

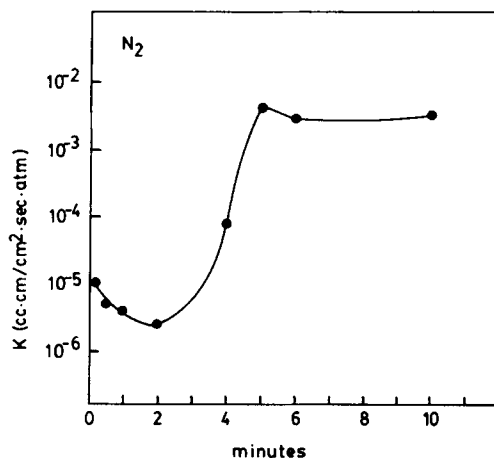


Fig. 5. Acetone evaporation time effect on gas permeabilities.

where  $M_2$  and  $M_1$  are molecular weights for heavy and light gases, respectively.

## RESULTS AND DISCUSSION

### Effects of the Membrane Preparation Process on Permeability and Separation Factor

**Permeability.** In the previous section, the membrane casting process was discussed. If the membrane casting conditions are changed, permeabilities will be influenced. Among them, the dope solution mixing ratio, acetone evaporation time, heat treatment temperature, and the freeze-drying conditions are important factors to determine the membrane structure which has an effect upon gas permeability. First of all, a standard sample was prepared according to the following conditions. (1) A mixed solution was of cellulose acetate, acetone, and formamide in the ratio of 5:9:6 by weight. (2) Evaporation time was 30 s. (3) Immersed time in cold water was for 1 h. (4) Heat treatment time was 10 min at 80°C. (5) The freeze-dried condition was not changed, as shown in the previous section. This standard sample was the same as freeze-dried commercial reverse osmosis membrane. Then, an attempt was made to find a membrane with highest flux by changing the membrane process condition. First, only heat treatment temperature was changed from 20°C to 90°C for constant 10-min heat treatment time. In Figure 4, permeabilities  $K$  for Ar and Kr gases are plotted against heat treatment temperature.  $K$  showed a peak at 80°C. In the successive membrane process, the heat treatment temperature was fixed at 80°C. Second, the acetone evaporation time was varied from 15 s to 10 min. In Figure 5, permeability  $K$  for  $N_2$  is plotted against the acetone evaporation time.  $K$  decreased between 15 s and 2 min. On the contrary,  $K$  increased abruptly between 2 min and 4 min.

**Separation Factor.** In this section, the relation between separation factor and the membrane preparation process is discussed, using mixed  $N_2$  and Kr gases. In the previous section it is suggested that acetone evaporation time and

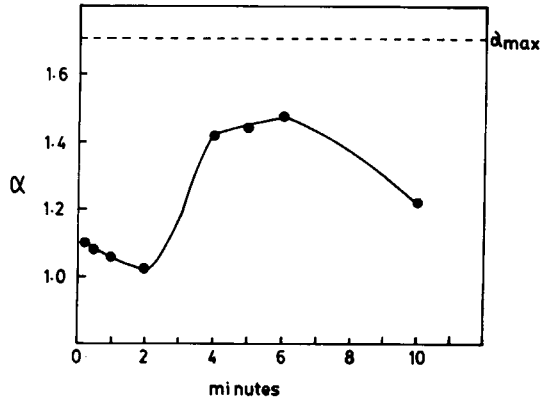
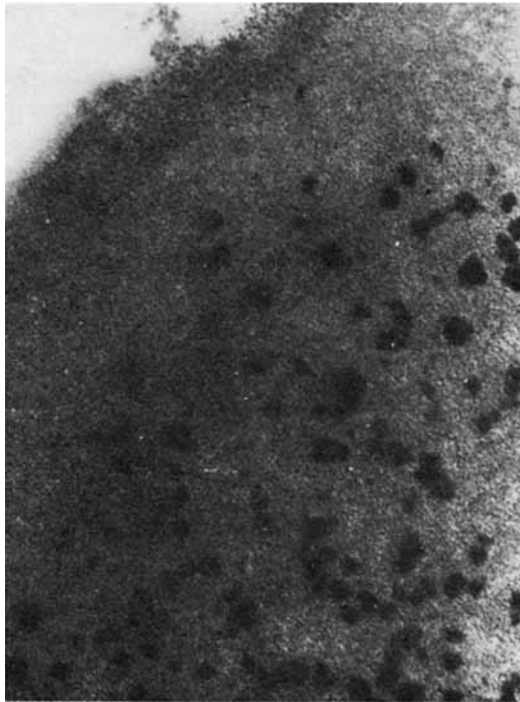


Fig. 6. Acetone evaporation time effect on  $N_2$ -Kr separation factors.

freeze-drying condition were the very important factor to obtain a high flux membrane. In Figure 6 the separation factors are against the acetone evaporation times. The separation factor was very small between 15 s and 2 min evaporation time. In this region, permeability was also small. The separation factors increased abruptly between 2 min and 4 min acetone evaporation time, where permeability also increased. The separation factor took constant values



0.2  $\mu\text{m}$

Fig. 7. Lead citrate staining, ultrathin sectioning of electron micrograph of surface in freeze-dried cellulose acetate membrane.

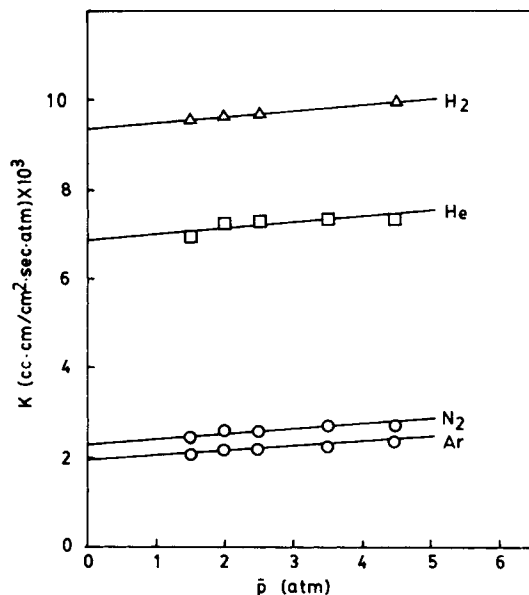


Fig. 8. Gas permeabilities as a function of mean pressure.

at more than 4 min and decreased at 10 min. If the flow through this membrane is ideal Knudsen flow, the separation factor becomes 1.73 for  $N_2$  and Kr, which is shown as dotted line in Figure 6. The measured factor was 1.43. Heat treatment temperature was varied from  $65^\circ\text{C}$  to  $95^\circ\text{C}$  for membrane whose acetone evaporation time was 5 min. But the separation factor was not affected. Even if the formamide content was increased to 35% in dope solution, the separation factor also was not markedly changed. These indicate that the membrane structure is mainly confirmed during freeze drying at a fixed dimension.

These results are very interesting, because the separation factor was improved according to the increase of permeability. In Figure 2 tension increased abruptly in the earlier stage of drying time on account of the water evaporation from pores. The successive stress-relaxation suggests that the rearrangement of pore size distributions occurred in order to get a optimum pore size for gas separation.

### High Flux and High Separability Membrane

We could prepare the porous membrane which has high flux and high separability as cited above. For such a membrane we will discuss the structure and gases permeabilities and separabilities in this section.

**Membrane Structure.** The membrane structure was observed with an ultrathin sectioning microscope.<sup>9</sup> Before observation the sample was strained by lead citrate. Figure 7 shows a high-magnification electron micrograph of the top surface. The dark parts indicated Pb compounds produced by the reaction of cellulose acetate and lead citrate. They were deposited in pores with diameters of about  $50 \text{ \AA}$ . It was found that the fine structure of the top surface of this membrane was a network that considered of about  $50 \text{ \AA}$  pores and another existing among pores in the porous substrate.

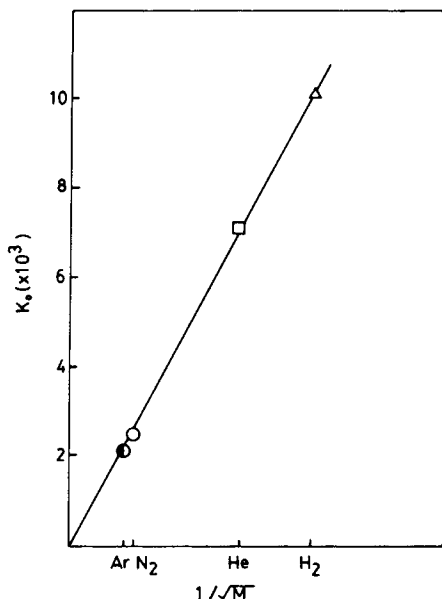


Fig. 9. H<sub>2</sub>, He, N<sub>2</sub>, and Ar permeabilities  $K_0$  vs. inverse square root of molecular weight  $M^{-1/2}$ .

**Gas Permeability.** In Figure 8 the permeabilities of H<sub>2</sub>, He, N<sub>2</sub>, and Ar gases were plotted against the mean pressure. They depend on the pressure and decrease according to the increasing molecular weight of gases, which confirms that this membrane is porous. The permeability coefficient is expressed by<sup>10,11</sup>

$$K = K_0 + (B_0/\eta)\bar{p} \quad (6)$$

Here  $K_0$  is the Knudsen permeability coefficient, which is inversely proportional to the square root of the molecular weight  $M$  of the gas,  $\eta$  is the viscosity of the gas, and  $B_0$  is a geometrical factor of the membrane. The coefficient  $K_0$  can be estimated by an extrapolation of  $K$  vs.  $\bar{p}$  to  $\bar{p} = 0$ , and  $B_0/\eta$  is obtained from the slope. The value of  $K_0$  thus obtained is plotted against  $M^{-1/2}$  in Figure 9, and  $B_0/\eta$  is plotted against  $1/\eta$  in Figure 10. Both were linear and the mean pore size  $\bar{r}$  in the membrane was evaluated by use of the relation<sup>12,13</sup>

$$\bar{r} = (B_0/K_0)(16/3)(2RT/\pi)^{1/2}M^{-1/2} \quad (7)$$

with

$$K_0 = (4/3)(\delta/k_1q^2)\epsilon\bar{r}(8RT/\pi M)^{1/2} \quad (8)$$

$$B_0 = \epsilon\bar{r}^2/kq^2 \quad (9)$$

where  $\delta/k_1 = 0.8$  for all membrane,  $q$  is the tortuosity factor,  $R$  is the gas constant,  $T$  is the absolute temperature,  $\epsilon$  is the porosity,  $M$  is the molecular weight of the permeant, and  $k = 2.5$  for all membranes. The apparent mean pore size (radius) thus calculated was about 60 Å. This value agrees approximately with the value observed with an electron microscope. Effective porosity  $\epsilon/q^2$  was calculated from eq. (8) or (9) and listed in Table I with N<sub>2</sub> gas permeability ( $K$ ), mean pore size ( $\bar{r}$ ) and void volume. The void volume is defined as the fraction of the



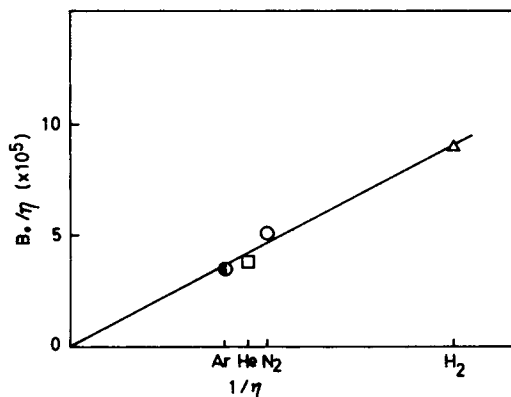


Fig. 10.  $B_0/\eta$  of  $H_2$ , He,  $N_2$ , and Ar vs. inverse viscosity of these gases  $1/\eta$ .

membrane volume which is not occupied by the polymer. The low value of  $\epsilon/q^2$  compared to those of the void volume indicate either a very high tortuosity factor or a large number of dead end pores. The ratio between the void volume and the effective porosity  $\epsilon/q^2$  is equal to 12.2. If no dead-end pores existed in this film,  $q^2$  would have been 12.2, an extremely high value considering that the tortuosity factor of a consolidated spherical material is assumed to be less than 2 from statistical considerations. If we assign to  $q^2$  a value of 2, it implies that 75.6% of the void volume is not active.

**Gas Separation.** As shown in the previous sections, separation factor for  $N_2$  and Kr got a good value, and the Knudsen flow rules the flow mechanism for this membrane. It is possible to separate various mixed gases, especially those which have little interaction with membrane.<sup>14-17</sup> An attempt was made to separate mixed gases  $H_2$ -He, Ar-Kr,  $N_2$ -Kr, He-Ne,  $H_2$ -Ne, He-Ar, Ar- $H_2$ , He-Kr, Ar-He, and He- $H_2$ . Table II shows separation factors as a function of the pressure on the high pressure side. Mixed gases combinations are listed in the first column. The concentration of the former gas was 99.5%, which was called the base gas. Therefore, the separation factor means condensation factor of lighter gas.  $\alpha_0$  indicates the ideal separation factor, which equals the square root of the ratio of heavy gas molecular weight to light one. If Knudsen flow dominates in the membrane, separation factor approaches to  $\alpha_0$ .  $\alpha$  increases with high pressure side pressure  $p_F$  and smaller than ideal values  $\alpha_0$ . The last two rows show an opposite gas concentration as  $H_2$ -He and He-Ar, i.e., concentration of He and Ar are 99.5% in the combination of He- $H_2$  and Ar-He, respectively. From  $\alpha$  and  $\alpha_0$  separation efficiency is expressed by (see Appendix<sup>18</sup>)

$$Z = (\alpha - 1)/(\alpha_0 - 1) \quad (10)$$

TABLE I  
Permeability Coefficient of  $N_2$  Gas, Mean Pore Size, Porosity, and Void Volume

Permeability $K_{N_2}$ (cc-cm/cm <sup>2</sup> -s-atm)	Mean pore size (radius) $\bar{r}$ (Å)	Effective porosity ( $\epsilon/q^2$ ) $\times 10^2$	Void volume (%)
$2.85 \times 10^{-3}$	60	7.6	93

TABLE II  
Separation Factors for Freeze-Dried Cellulose Acetate Membrane

Mixed gases	$\alpha_0 = \sqrt{M_2/M_1}$	$p_F$ (pressure on high pressure side (kg/cm <sup>2</sup> ·G))				
		1.0	2.0	3.0	5.0	7.0
H <sub>2</sub> -He	1.41	1.14	1.15	1.17	1.19	1.20
Ar-Kr	1.45	1.20	1.25	1.29	1.23	1.29
N <sub>2</sub> -Kr	1.73	1.32	1.39	1.43	1.42	1.39
He-Ne	2.25	1.63	1.98	1.92	1.96	2.00
H <sub>2</sub> -Ne	3.16	1.88	2.20	2.27	2.32	2.33
He-Ar	3.16	2.07	2.26	2.35	2.14	2.58
Ar-H <sub>2</sub>	4.34	2.64	2.67	3.58	3.07	
He-Kr	4.58	2.81	3.44	3.68	3.66	3.55
He-H <sub>2</sub>	1.41	1.11	1.13	1.17	1.19	1.19
Ar-He	3.16	1.63	1.97	2.12	2.37	2.52

$Z$  is plotted in Figure 11 as a function of pressure. If the gas flow in the membrane is ideal Knudsen flow  $Z$  will be 1. As shown in Figure 11 and eq. (6), the flow through this cellulose acetate membrane is not only the ideal Knudsen flow, but also contains a little viscous flow. It is considered that this is one of the reasons why the  $Z$ 's are not unit.  $Z$  values strongly depend on the combinations of gases.  $Z$  shows that the separation between two different inert gases has high efficiency better than that between two atoms molecule gas and inert gas. Therefore we should consider the effects by not only viscous flow<sup>6</sup> but also surface flow.<sup>19</sup>

## APPENDIX

If the flow through membrane is ideally Knudsen flow, a component molar velocity is proportional to the difference in partial pressure between inflow and outflow:

$$G_1 = A_{G_1}(p_F x_F - p_B x_B) = A_{G_1} \cdot p_F (x_F - \gamma x_B) \quad (11)$$

$$\begin{aligned} G_2 &= A_{G_2}[p_F(1 - x_F) - p_B(1 - x_B)] \\ &= A_{G_2} \cdot p_F [(1 - x_F) - \gamma(1 - x_B)] \end{aligned} \quad (12)$$

where  $\gamma = p_B/p_F$  and  $p_F$  and  $p_B$  are pressures on the high and low pressure sides, respectively.  $x_F$  and  $x_B$  are the molar fractions of component 1 in high and low pressure sides, respectively.  $A_{G_1}$  and

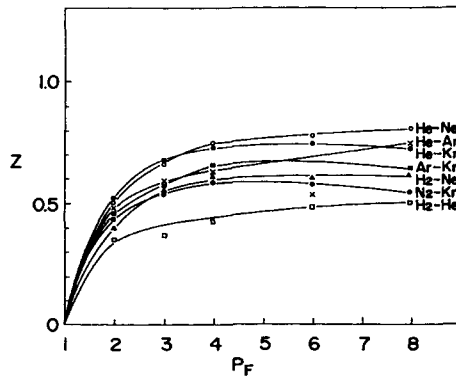


Fig. 11. Separation efficiency for various mixed gases as a function feed gas pressure.

$A_{G_1}$  and  $A_{G_2}$  are permeabilities of pure gases for components 1 and 2, respectively, and are written as follows:

$$A_{G_1} = a/(M_1)^{1/2}, \quad A_{G_2} = a/(M_2)^{1/2} \quad (13)$$

where  $a$  is constant. The separation factor is defined as

$$\alpha = (x_B/1 - x_B)/(x_F/1 - x_F) \quad (14)$$

In this experiment, the light gas molar fraction on the low pressure side is defined as

$$x_B = G_1/(G_1 + G_2) \quad (15)$$

From eqs. (11), (12), and (15), the following relation is formed between  $x_F$  and  $x_B$ :

$$x_B/1 - x_B = G_1/G_2 = \alpha_0(x_F - \gamma x_B)/[(1 - x_F) - \gamma(1 - x_B)] \quad (16)$$

When pressure on the low pressure side is very small, ( $p_B/p_F \rightarrow 0$ )

$$\frac{x_B}{1 - x_B} \bigg/ \frac{x_F}{1 - x_F} = (M_2/M_1)^{1/2} = A_{G_1}/A_{G_2} = \alpha_0 \quad (17)$$

If ideal separation factor  $\alpha_0$  is defined, molar fraction on the high pressure side is confirmed at  $x_F^0$  and from eq. (17)

$$x_F^0 = x_B/[x_0 + \alpha_0(1 - x_B)] \quad (18)$$

Here, separation efficiency  $Z$  is defined as

$$Z = (x_B - x_F)/(x_B - x_F^0) \quad (19)$$

$x_F$  and  $x_F^0$  from eqs. (16) and (18) are substituted into eq. (19):

$$Z = 1 - \gamma \quad (20)$$

Equation (20) indicates that separation efficiency will be decreased only back flow from the low pressure side, if the flow is ideally Knudsen flow. When  $x_F$  and  $x_F^0$  from eqs. (14) and (18) are substituted into eq. (19),

$$Z = (\alpha - 1)[x_B + \alpha_0(1 - x_B)]/(\alpha_0 - 1)[x_B + \alpha(1 - x_B)] \quad (21)$$

In these experiments,  $x_F = 0.995$ ,  $1 - x_F = 0.005$  and  $(\alpha_0/\alpha) < 5$

$$[x_B + \alpha_0(1 - x_B)]/[x_B + \alpha(1 - x_B)] \simeq 1$$

Then eq. (21) becomes

$$Z = (\alpha - 1)/(\alpha_0 - 1) \quad (22)$$

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