

Studies on
a thermal method of gas separation with porous membrane

Shoeji Nakaye

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Chapter 1

General Introduction

The separation of mixture is a process of mass transfer caused by the motion of molecules, in which a mixture of substances is converted into mixtures whose one or more components are enriched. In case of gases, utilizing the phenomena stemming from the motion of gas molecules, one has an opportunity to control the mass transfer as desired. One of such methods and its application are demonstrated in this thesis.

The motion of gas molecules affects properties of gases. The molecules move around and collide with each other, transporting their own mass, momentum and energy. The effects of their diffusion appears as molecular diffusion in gas mixtures, viscosity, or heat conduction.

However, we do not need to consider the molecular motion when the gas is equilibrated by frequent collisions between gas molecules. In this case, the gas can be modeled as a continuous mass, and the effects of the molecular motion can be represented through corresponding coefficients: diffusivity, viscosity or thermal conductivity. This lead to the suitability for describing the fluid motion by equations of fluid dynamics.

On the other hand, for gases with less intermolecular collisions, there emerge the effects of the molecular motion. The gas in such situation is called the rarefied gas or the molecular gas, and its behavior is described using the kinetic theory of gases. Low frequency of collisions means that the molecules travel significant distances between intermolecular collisions, and its effects —the rarefied effects of gases— lead to phenomena characteristic to the rarefied gas. Amongst the phenomena are flows induced by temperature fields and Knudsen diffusion of mixtures, as well as the non-equilibrium behavior of gases near the boundary or in the shock waves.

To begin with, the flows induced by temperature fields are described. While a gas molecule travels without colliding with others, its kinetic energy is kept constant at the energy depending on the temperature at its starting point. Since the velocity distribution of molecules at some point is resultant from the temperature distribution around there, the non-uniform energy or temperature distribution leads various gas flows in the rarefied gas. Recent studies on the rarefied gas clarified various kinds of gas flows induced by temperature fields [1]. One of them is the thermal transpiration,

and it has been extensively studied both for pure gases and for their mixtures [2–15]. The flow is induced through a tube, where the temperature varies along its axis. The rarefied gas in the tube flows from the cold part to the hot part according to their temperature difference, whose flow speed is related to the thermal speed of molecules.

An application of thermal transpiration flow is the Knudsen pump [16], which features a simple structure without any mechanical part. It is only recently that a Knudsen pump was reported to work at atmospheric pressure using porous membranes [17]. Inducing the thermal transpiration at atmospheric pressure had been difficult because sufficient temperature difference must be provided in a scale of 100 nm, which is comparable to the mean free path of atmosphere. This difficulty had been overcome using MCE (mixed cellulose ester) membranes with 25–100 nm sized pores, held between two metal plates: one is heated and the other is maintained close to the room temperature. These metal plates have 100- μm -depth ditches on their surfaces to secure the space for gases to flow outside the membrane, while conducting heat to the surface of the membrane. This development enables the thermal transpiration to be easily induced even at a pressure as high as the atmospheric pressure.

An application of another effect, Knudsen diffusion, can be found in the gas separation process using porous membrane [18]. When a gas flows through a so narrow channel that gas molecules collide with the pore walls instead of with each other, the absence of the intermolecular collision leads to a difference in the speed of gas components flowing through the channel. Then, driving a flow through a porous membrane by a pressure difference, separation occurs during the permeation of gases through the narrow pores of the membrane. However, the complete separation is far beyond the power of the Knudsen diffusion because all components permeate through the membrane in the same direction.

It is noted that there are two driving forces of the gas flow mentioned above: temperature difference and pressure difference. Their combination brings an interesting result, when the pore diameter is comparable to the mean free path. In this case, the pressure-driven flow has almost no dependence of flow speeds on gas species unlike the Knudsen diffusion of gases in much narrower channel. In contrast, the flow speed of the thermal transpiration flow depends on gas species according to the thermal speed of gas molecules. In addition, the speeds of these two flows remain in the same order [13]. Therefore, since each one of the driving forces can be controlled by a different physical parameter, two physical quantities of permeate flow is controllable [19]. Consequently, for the binary mixture of gases, the combination is a way to independently control the permeation speed of each component. It is even possible to realize the molecular exchange flow, where one component flows through the membrane in the opposite direction of the flow of the other component, by balancing the temperature and the pressure difference across the membrane.

In spite of its utility, the molecular exchange flow has never been observed. The effect is so small that it has to be amplified for the detection of the effect itself, because

of the limitation in the temperature difference applicable to the membrane. The counter flow setup is adopted in order to amplify the effect, which is similar to the hollow fiber membrane gas separation unit.

The realization of the molecular exchange flow is indispensable for the advancement of the membrane gas separation technique. The origin of the membrane gas separation goes back at least to the nineteenth century, when Thomas Graham measured the permeation rates of gases through various diaphragms and porous media [20, 21]. The separation method emerged as an industrial field in twentieth century along with the advancement in the membrane fabrication [22–24]. Throughout its history, whether or not the separation process depends on the Knudsen diffusion, the membrane gas separation has one principle in common: separating gas mixtures based on the difference of the permeation speeds of gas components; In other words, all components permeate in the same direction. This have been hindering the application of the membrane gas separation to obtaining high purity gases. The molecular exchange flow can conquer the restriction derived from the principle of the ordinary membrane gas separation.

In chapter 2, I propose a design of a device for inducing the molecular exchange flow and accumulating the effect. The device is designed to provide a porous membrane with a temperature difference between its surfaces. With the temperature difference and an externally provided pressure difference, the molecular exchange flow is induced through the membrane. The effect is accumulated by the flow in the device to generate an observable variation of mole fraction. The design is investigated using a simplified method of numerical simulation, and then demonstrated experimentally. This is the very first report on the observation of the molecular exchange flow.

In chapter 3, a gas separator system is proposed, which makes use of the molecular exchange flow and requires a temperature difference as its only energy source. The pressure difference for the molecular exchange flow is provided by the thermal transpiration through a membrane, instead of being provided externally as in the previous chapter. The feasibility of the proposed design as a novel method of membrane gas separation is numerically investigated. In chapter 4, a separator system base on this design is fabricated and experimentally demonstrated.

Finally, this thesis is concluded in chapter 5.

Chapter 2

Demonstration of Molecular Exchange Flow

2.1 Introduction

Gas separation by membranes is an attractive method, because of its simple device structure, easy operation, and high energy efficiency. A great number of research efforts have been made for the fabrication of separation units and of membranes with appropriate macroscopic and microscopic structure, including the design of molecules of the membrane [23–26]. These various implementations of membrane separation have a common simple principle: the feed is supplied to one side of the membrane at higher pressure relative to the other side, and the gas molecules permeate according to the pressure difference. The separation occurs with the dependency of the permeation speed on molecular species. The dependency comes from the fact that the mechanism of molecular transport in the membrane is quite different from that in bulk gas: various diffusion effects, such as Knudsen diffusion, molecular sieving, and solution diffusion, play important roles. In these implementations, we can control only one driving parameter for the molecular transport – the pressure difference across the membrane. It means that only one physical quantity of permeate flow is controllable, which may be the total molecular flux of the mixture through the membrane. As a result, it is impossible to control the ratio of molecular fluxes of component gases; the performance of gas separation is mostly determined by the physical and chemical properties of the membrane.

The above use of membranes, however, utilizes only a part of the ability of membranes. That is, the pressure difference is not the only driving force of molecular transport in membranes. According to the results of molecular gas dynamics, which deals with the behavior of the gas with a finite mean free path of gas molecules, temperature fields may induce various steady gas flows other than natural convection [27]. These flows vanish in the continuum (i.e., small mean free path) limit, but they remain appreciable in the rarefied gas, where the length of the mean free path of gas molecules is comparable to the scale of the system. The rarefied condition applies to the gas in

micro-channels of porous membrane if the pore diameter is comparable to the mean free path. For such porous membranes, there are two driving forces for gas flow in the membrane, which can be controlled independently by two different physical parameters – pressure and temperature differences across the membrane. In this case, we can control two physical quantities of permeate flow. In the case of binary mixtures, molecular flux of each component can be controlled independently [19]. Thus the selectivity of a given membrane is controllable. It is even possible that one component flows in the opposite direction of the flow of the other component. This is one of the keys to the thermal enhancement of membrane gas separation presented in this thesis.

Although there are various kinds of flows induced by temperature fields, only a few of them can be used owing to the limitations in fabrication. The local flow speed of thermal edge flow [28, 29] is proportional to the square root of the mean free path, but the requirement for the shape of micro-channel is not simple. As for the flows whose speed is proportional to the mean free path, two types of flow are investigated: the nonlinear thermal stress flow [30] and the thermal transpiration (or thermal creep) flow [2, 3]. The former requires a larger variation of temperature, which is difficult to achieve in the membrane. The latter is well known linear effect, and is extensively studied by many researchers, including the case for gas mixtures [2–12, 14]. (Please refer reviews [15, 31, 32] for extensive references.) The studies lead the development of the pump with no moving parts – Knudsen pump [16]. In 2011, Gupta and Gianchandani [17] succeeded to induce the thermal transpiration flow at atmospheric pressure by using a MCE membrane. Their dime-sized pump induces appreciable gaseous flux around 1 sccm ($1 \text{ cm}^3/\text{min}$ at standard temperature and pressure) and a pressure difference around 1 kPa with a temperature difference of 30 K. The pump is also stable enough to work continuously over 6 months. It is one crucial step for membrane technology to utilize the thermal transpiration flow. I develop the gas separation devices in this thesis using their innovative design of the pump for reference.

The purpose of the device is to demonstrate the enhancement of membrane separation by temperature field. The native gas separation effect of small portion of MCE membrane with temperature difference around 30 K is, of course, expected so small for engineering purposes. Some improvements are required to amplify the effect; e.g., the use of a long tube [33] or a series connection of Knudsen pumps [34]. For the improvement, I use the counter flow setup similar to the hollow fiber membrane gas separation unit [23]. This is the second key to the present work, which enables the detection of the thermal enhancement of membrane separation. Firstly numerical simulations are carried out on the gas flow in the test device to confirm the effect of the combination of the thermal enhancement and the counter flow setup. Secondly I will experimentally demonstrate the new method of membrane gas separation with binary mixtures of noble gases.

2.2 Structure of Gas Separator

2.2.1 Concept

The schematic of the gas separator [35, 36] is shown in figure 2.1. The device consists of a porous membrane with micro-channels and two channels (F and R) along the both sides of it. The channel F is connected to the channel R at the end to form a U-bend. Feed gas, a binary gas mixture of smaller molecules A (mass of a molecule m^A) and relatively larger molecules B (mass m^B), is introduced into the device through the inlet. The mixture mainly flows through the channel F, the U-bend, and the channel R toward the outlet, while some part of the mixture flows through the micro-channels in the membrane. The nature of the latter flow differs from that of the flows in channel F and R, because the flow is in the rarefied gas regime. There, the molecular transport generally depends on species or molecular mass, and the temperature field induces a distinctive flow of rarefied gas [27], which can be controlled by the difference between the temperature at channel F (T_F) and that at R (T_R). As is described in the next paragraph, it is possible that the smaller molecules A flow in the direction of R to F, while the larger molecules B flow from F to R. These species dependent flows lead to a variation of the composition of the gas in channel F and R around each individual micro-channel. Let us consider the variation of mole percentage χ in channel F and R, which is defined by

$$\chi = \frac{100n^A}{n^A + n^B},$$

where n^α ($\alpha = A, B$) are the number densities of α -molecules. An increase of χ in channel F leads to the decrease of χ in R and vice versa, if the difference of χ between channel F and R is small. These variations of mole percentage χ are convected downstream of channel F and R. When all micro-channels give similar impacts on χ , a gradient of χ along the membrane will be induced by the accumulation. The counter flow setup in channel F and R is devised for this purpose. In this arrangement, the signs of the variations of χ along the membrane are the same in channel F and R. This helps the

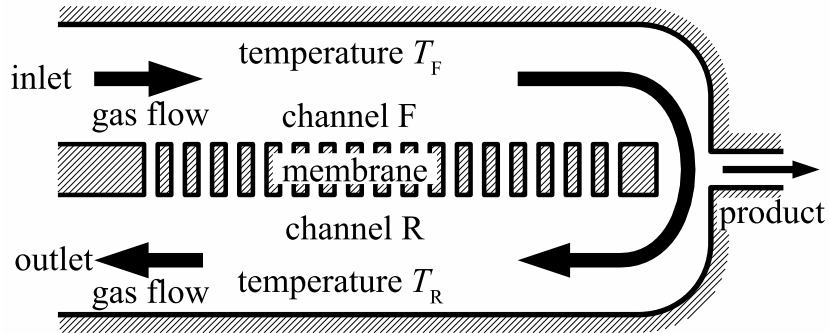


Figure 2.1: Schematic of the gas separator.

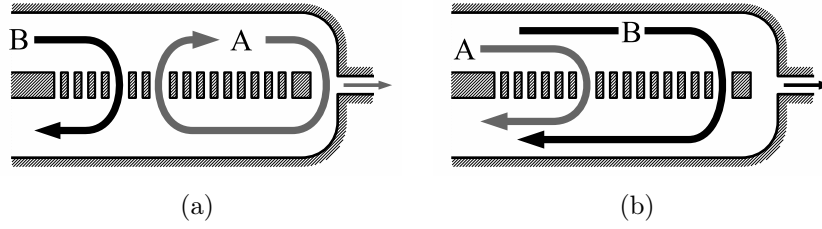


Figure 2.2: Behavior of the component gas in the gas separator. A: gas with smaller mass of a molecule; B: that for larger mass of a molecule. (a) $T_F/T_R > 1$; (b) $T_F/T_R \leq 1$.

difference of χ between F and R keep small over entire surface of the membrane so that diffusion in the micro-channels does not hinder the flows in the micro-channels. The gradient of χ along the membrane means that a gas component is concentrated at the part of U-bend. The product of the device is a small amount of gas taken from the U-bend part.

Now I discuss the rarefied gas flow through individual micro-channels. Since the flow speed in the micro-channel is small, linear theory of the Boltzmann equation applies and the flow is shown to be induced by the gradients of pressure, temperature, and mole fraction [7]. The pressure driven flow corresponds to the Poiseuille flow, where the gas flows in the direction opposite to the pressure gradient. The thermal transpiration is the flow in the direction of the temperature gradient. The last one is the effect of diffusion. Here I estimate the gas flow in the micro-channel induced only by the pressure and temperature gradients, since, as is described in the previous paragraph, the difference of mole percentage χ between F and R is small in normal operations of the present device. Firstly I consider the case where the value of the temperature ratio T_F/T_R is close to that of the pressure ratio p_F/p_R (p_F : pressure at the inlet, p_R : pressure at the outlet. Note that $p_F/p_R > 1$). The thermal transpiration occurs in the direction of $R \rightarrow F$, and the pressure driven flow is in the direction of $F \rightarrow R$. The main parts of these flows cancel out each other due to the condition $T_F/T_R \approx p_F/p_R$, and the species dependence of the flows becomes important. For the temperature driven flow, A-gas flows faster than B-gas, and the speed ratio is given approximately by the speed ratio of the molecules $\sqrt{m^B/m^A}$. This reflects the fact that the thermal transpiration is characteristic to rarefied gas and is the effect of the free motion of molecules [1]. The situation is different for pressure driven flow. The speed ratio is $\sqrt{m^B/m^A}$ only in the Knudsen (or large mean free path) limit. It approaches unity in the continuum limit where the free motion of molecules is intercepted by intense intermolecular interactions. The speed ratio generally takes intermediate value between unity and $\sqrt{m^B/m^A}$. This difference between the speed ratios of the two flows is important – it enables arbitrary speed ratio between A-gas and B-gas in the linear combination of temperature and pressure driven flows. In the present setup $T_F/T_R \approx p_F/p_R > 1$, A-gas tend to flow in the direction of $R \rightarrow F$, more than B-gas. It is even possible that A-molecules move in the direction $R \rightarrow F$ while the same number of B-molecules move in the direction $F \rightarrow R$ under an appropriate value of the gradients of pressure and temperature along

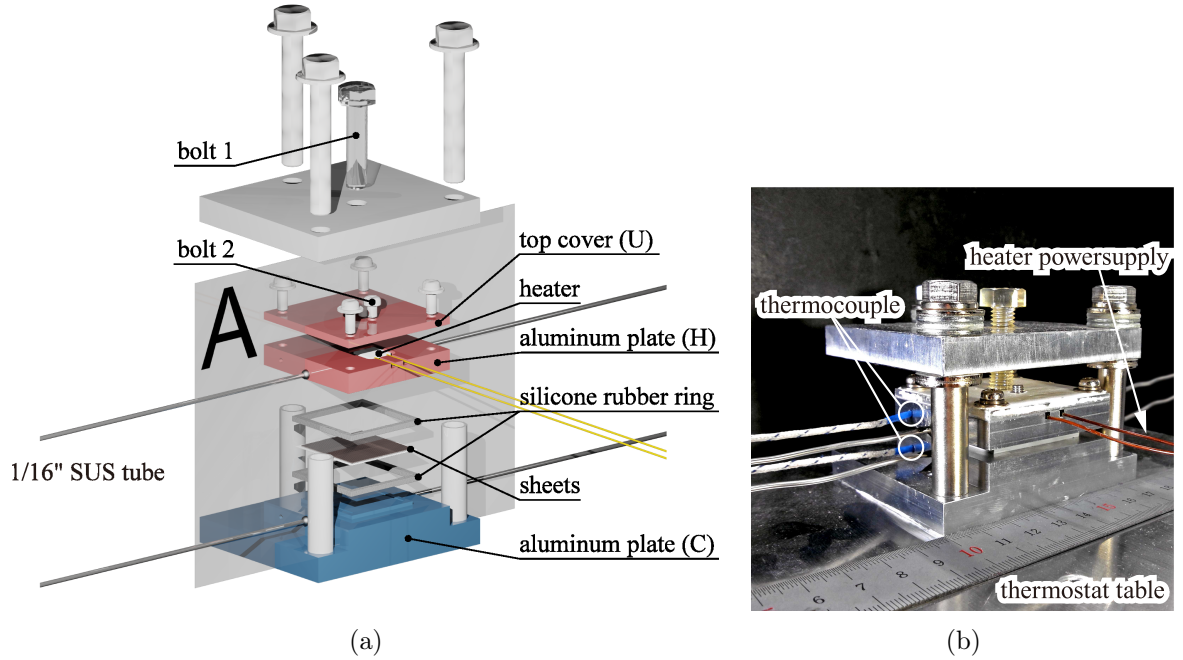


Figure 2.3: (a) Exploded view of the device. (b) The photograph of the device. The cross section at plane A of the device is shown in figure 2.4(b).

the micro-channel [19]. Hereafter this state is referred to as “molecular exchange”. If the pressure gradient is larger (smaller) than the appropriate value, the flows are accelerated in the direction of $F \rightarrow R$ ($R \rightarrow F$). Nevertheless A-gas has larger velocity in $R \rightarrow F$ direction. Finally, I consider other cases, where $T_F/T_R \leq 1$ or the thermal transpiration is very weak. In these cases, both of A-gas and B-gas flow in the direction $F \rightarrow R$, and the speed is larger for A-gas. The thermal transpiration enhances the effect of pressure-driven flow.

The behavior of the each component gas in the present device is exaggerated in figure 2.2. The panel (a) shows the case of $T_F/T_R > 1$. The B-molecules are exhausted from the device by the flow $F \rightarrow R$, while some part of A-molecules circulate around the U-bend part by the flow $R \rightarrow F$ through the membrane. Therefore, A-gas is concentrated in the product gas. The panel (b) shows the case of $T_F/T_R \leq 1$. A-molecules are exhausted from the device earlier than B-molecules, and the product gas is B-rich. The case for $T_F/T_R = 1$ is the same as the membrane gas separator by Knudsen diffusion. The thermal transpiration flow in $F \rightarrow R$ direction for $T_F/T_R < 1$ will intensify this effect.

The expression of the increment $\Delta\chi$ of the mole percentage of the product gas is obtained with the mass conservation as

$$\Delta\chi = \frac{(100 - \chi_I) Q^A - \chi_I Q^B}{Q_I + Q^A + Q^B},$$

where Q_I and χ_I are, respectively, the volume flux and mole percentage of the feed,

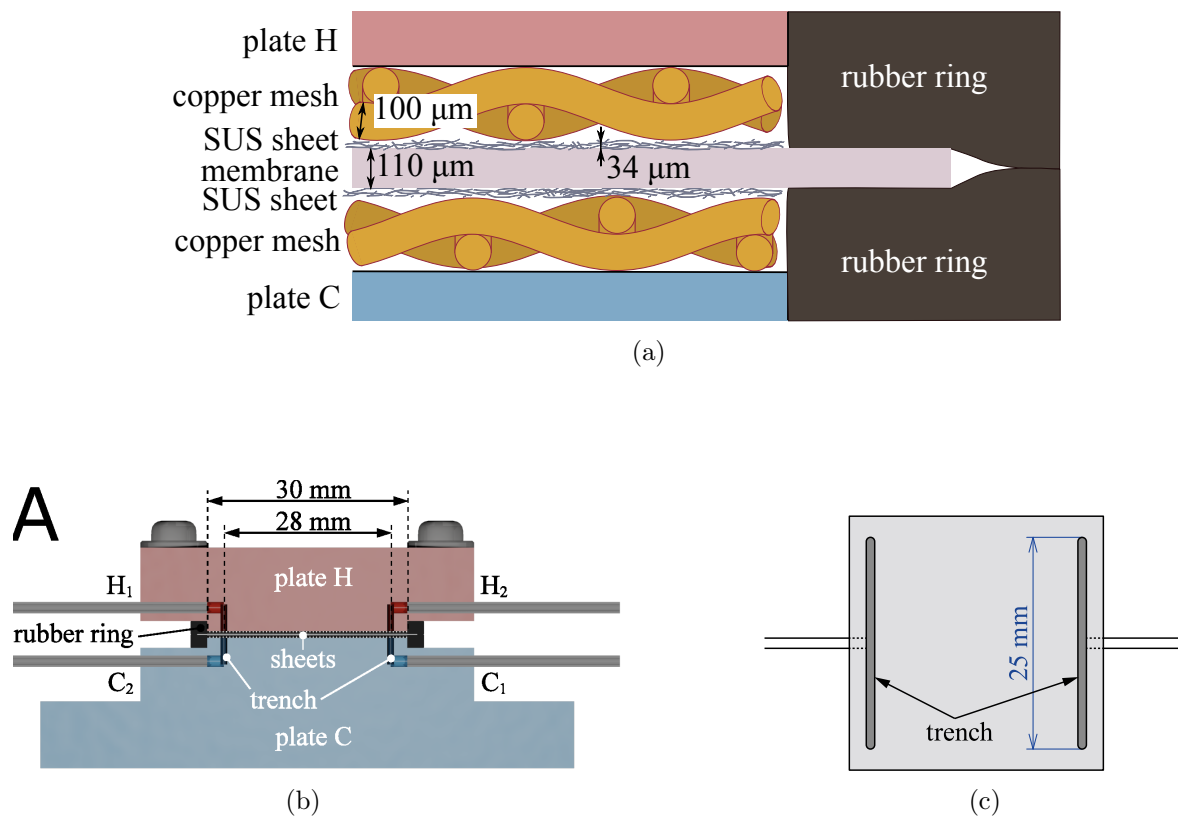


Figure 2.4: Cross sections of the device. (a) Close up of multilayered mesh structure. (b) Gas inlet and outlet system. (c) Top view of the stage for the sheets.

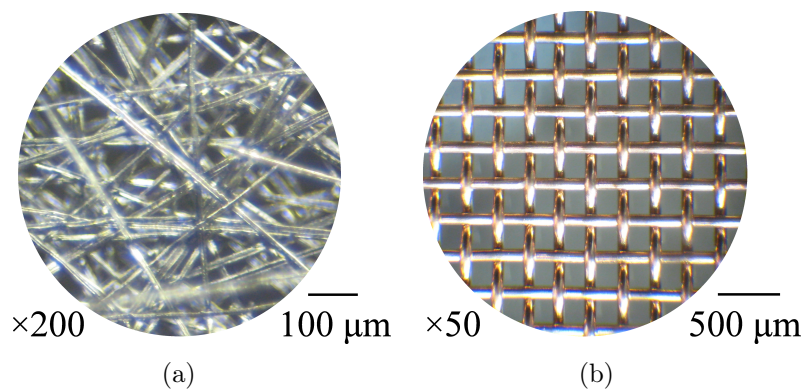


Figure 2.5: Photographs of the metal meshes used in the device. (a) Sintered SUS fiber sheet and (b) copper mesh.

and Q^α are the net volume flux of α -gas through the membrane in $R \rightarrow F$ direction. The sizes of Q^α depend on the flow speeds in micro-channel and partial pressures in F and R. In the case of $T_F/T_R > 1$, the condition $Q^A > 0 > Q^B$ is available that insures $\Delta\chi > 0$. In order to simplify the experimental procedure, I will try to establish the pure molecular exchange condition

$$Q^A + Q^B = 0, \quad (2.1)$$

in the present work.

2.2.2 Device Structure

The exploded view and the photograph of fabricated device are shown in figure 2.3. The cross section and close-up figures are also shown in figure 2.4. Two aluminum plates H and C sandwich several sheets including the thermal transpiration membrane, which are described later. A small heater unit [$10 \times 10 \times 1$ mm, Micro Ceramic Heater MS-3 (Sakaguchi E.H VOC Corp.) with rated heating power 40 W] is attached between plate H and the top cover U (aluminum, $50 \times 50 \times 3$ mm). Heat-dissipating silicone grease is applied between the heater and plate H, and the heater is held against the plate H. The heat supplied by the heater is removed from plate C, which will be mounted on the thermostat table as shown in figure 2.3(b). The temperatures of plate H (T_H) and C (T_C) are measured by thermocouples shown in figure 2.3(b). Then I install the sheets including the membrane between plates H and C. The thermal transpiration membrane is a MCE membrane (Advantec MFS Inc. A010A047A). The pore size, thickness, and porosity of the membrane are $0.1 \mu\text{m}$, $110 \mu\text{m}$, and 65 %, respectively. The size of the membrane is 33×33 mm. This is a standard filter membrane, and about 10^3 times thicker than those used in usual membrane gas separation. Two flow channels F and R along the membrane are required according to the concept given in section 2.2.1. The flow channels are ensured by the multilayered mesh structure as in [37, 38]. That is, the MCE membrane is sandwiched between two sintered SUS fiber sheets (30×30 mm, thickness $34 \mu\text{m}$, and the porosity is around 80 %. Tomoegawa Paper Co. Ltd., Tomifleck SS8-50M) [see figure 2.5(a)], which is composed of short fiber of SUS316 with diameter $8 \mu\text{m}$. Then it is held between two copper meshes of size 30×30 mm [thread diameter $100 \mu\text{m}$, #100, see figure 2.5(b)]. The copper meshes provide the gas flow channel along the both sides of the membrane, which is protected by SUS sheets [figure 2.4(a)]. These metal meshes also provide the heat flux from plates H and C to the surfaces of the membrane. The edges of the membrane are sealed by two square silicone rubber square rings (outer size $35 \times 35 \times 2$ mm, inner size $30 \times 30 \times 2$ mm) as shown in the right end of figure 2.4(a).

The inlet and outlet for the gas flow are two trenches (25×1 mm, depth 4 mm) on the stage part of plates H and C [see figure 2.4(c)]. The gas is supplied and exhausted through the 1.7 mm diameter holes extended to the trenches in the plates H and C. For later convenience, inlets are identified by subscript 1 and outlets by 2 (e.g., H_1 is the inlet at plate H).

2.3 Performance Simulation

This is the first experimental work on the gas separation with the thermal transpiration through a membrane, and no result is known for this kind of device. Especially, the molecular exchange flow of the rarefied gas has never been confirmed experimentally. In this case, theoretical studies become important to confirm whether the fabricated device works as expected. Therefore, in this section, numerical analysis is carried out on the behavior of the mixture in the device. The analysis aim to determine the setup of the experiment, e.g., the connection of H_* and C_* ($*$ = 1, 2) ports of the device, and to estimate the qualitative features expected in the experiment, e.g., the variation of mole fraction.

The model of the gas separator device used in the numerical simulation is shown in figure 2.6. The model is 2D in X_1 - X_2 space, where X_1 -direction is taken along the membrane, which is replaced with an array of m micro-channels in the model (cf. figure 2.1). The width and length of each micro-channel is d and t , respectively. The spacing between the channels is d . The wall temperature in the micro-channel varies linearly from T_R (at channel R) to T_F (at channel F). The location of the array is $0 < X_1 < L = 2dm$. The channels R and F are slightly longer than L ; their ends are at $X_1 = -L_-$ and $L + L_+$. The width of both R and F is D . The feed gas is supplied to channel F at $X_1 = -L_-$. The mole percentage of smaller A-gas and temperature of feed mixture is, respectively, χ_1 and T_F . The gas is removed from channel F at the other end ($X_1 = L + L_+$). In the simple case with no production of gas, all of the gas is refluxed into channel R at $X_1 = L + L_+$, after regulating the temperature to T_R with some pressure drop p_D . The fluxes of α -gas at the inlet of R are determined by those at the outlet of F. The gas leaves the device at $X_1 = -L_-$ from channel R. The pressure, temperature, and number density of the mixture at the outlet are p_R , T_R and $n_R (= p_R / \kappa T_R, \kappa$: Boltzmann constant), respectively. In a calculation based on the kinetic theory, the length ℓ_R of the mean free path of gas molecules at a reference state is required to determine the impact of molecular collisions on gas motion. The mean free path of gas mixture is complicated since the lengths of free paths differ depending on the species of colliding molecules (e.g., A-A, A-B, and B-B pairs for binary mixture of A and B molecules). However, their ratios under some specific gas state are expressed by the parameters in intermolecular potentials, e.g., the diameter of molecule d_m^α ($\alpha = A, B$).

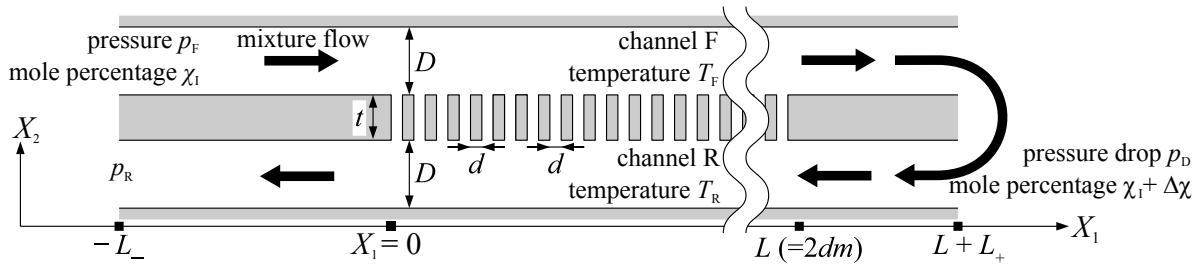


Figure 2.6: Numerical model of the device.

I define ℓ_R as the mean free path of pure A-gas at the stationary equilibrium state with number density n_R and temperature T_R . For hard-sphere molecules,

$$\ell_R = \left[\sqrt{2}\pi (d_m^A)^2 n_R \right]^{-1}. \quad (2.2)$$

Since I am interested in the phenomena in micro-channels, I specify ℓ_R by the Knudsen number in micro-channel:

$$\text{Kn} = \frac{\ell_R}{d}. \quad (2.3)$$

It is noted that Kn is not the degree of rarefaction for larger channels F and R. The local Knudsen number there is $\text{Kn}(d/D)$, which is much smaller than Kn since $d \ll D$. Incidentally, the relation between the mean free path and fluid properties such as viscosity is one of the basic problems in the kinetic theory and now enough informations are available for pure and mixture gases [1, 31, 39, 40]. For pure A-gas of hard-sphere molecules,

$$\nu^A \approx 0.563 \sqrt{\frac{2\kappa T_R}{m^A}} \ell_R, \quad (2.4)$$

where ν^A is the kinematic viscosity at pressure p_R and temperature T_R [1, 31]. Since the experimental values of viscosity etc. are available for pure gases, we can compare the analytical and experimental results through (2.2)–(2.4).

From the gas dynamic point of view, the gas flow in the above model consists of flows in two different regimes. The gas in the micro-channels is in the rarefied regime since the diameter of the micro-channel is of the order of the mean free path of the gas molecules. Since the driving mechanism of the present device relies on the phenomena characteristic to rarefied gas, the analysis with the Boltzmann equation is essential. Conversely the flows in channels R and F are in the continuum regime due to the large width of the channel. Although the Boltzmann equation is able to describe the gas in nearly continuum regime, precise numerical analysis for whole device is not possible with the Boltzmann equation because of the large width of the channels.

One of the solutions for analyzing the gas flow in this device is the “pipenet method” proposed in [35]. This is a method similar to one used to analyze the membrane gas separation performance [41] except for the micro-channel. In the pipenet method, I pay attention only to the longitudinal variations of the partial pressures p^α ($\alpha = A, B$) of component gases in channel R and F. The temperature of the gas is assumed to be uniformly T_R in channel R and T_F in channel F. The distribution of p^α is determined from mass conservation with the aid of the pre-constructed database [13] of rarefied flow through a channel. The details of the method are given in appendix A. In [35], the performance of a small device with 50 micro channels is analyzed by two approaches: the direct simulation Monte Carlo (DSMC) method [42] of the Boltzmann equation and the proposed pipenet method. It is shown that the pipenet method reproduces the DSMC results with significantly short CPU time (the ratio of CPU time $> 10^5$) so that the pipenet method is applied to estimate the performance of the present device.

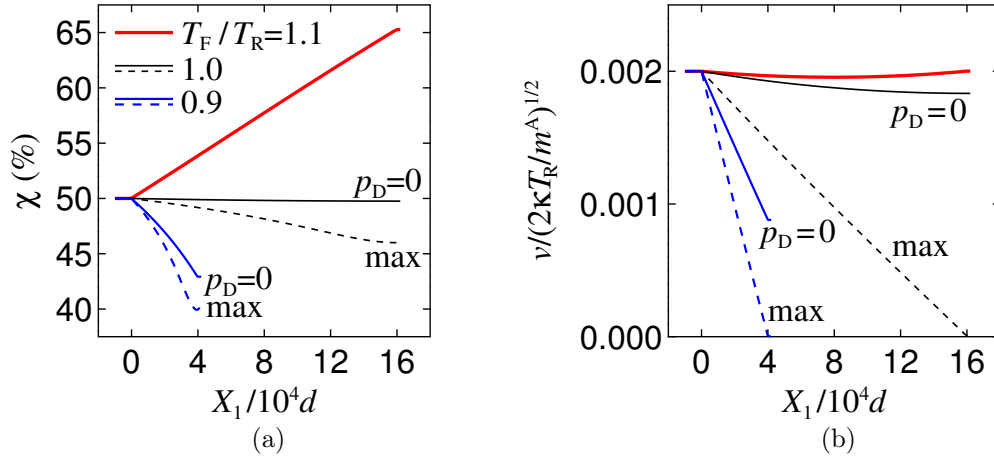


Figure 2.7: Result of numerical simulations for gas separators with $T_F/T_R > 1$ and $T_F/T_R \leq 1$. $m^B/m^A = 2$, $\text{Kn} = 0.5$, $t/d = 10^2$, $D/d = 2 \times 10^3$, and $v_F/c_R = 2 \times 10^{-3}$. The results for $T_F/T_R = 0.9, 1, 1.1$. Two extreme cases for p_D/p_R are shown for the cases $T_F/T_R \leq 1$. The distribution of (a) mole percentage χ of A-gas and (b) the flow velocity v of mixture in X_1 direction.

2.3.1 Gas separators for $T_F/T_R > 1$ and $T_F/T_R \leq 1$

Firstly I assess the possibility of two types of device given in section 2.2.1, $T_F/T_R > 1$ and $T_F/T_R \leq 1$, based on the results shown in [35]. The analysis is carried out for binary mixture of hard sphere molecules A and B with the same molecular diameter. The mass ratio $m^B/m^A = 2$, $\chi_I = 50\%$, $\text{Kn} = 0.5$, $t/d = 10^2$, and $D/d = 2 \times 10^3$. The simulation is carried out for $T_F/T_R = 0.9, 1, 1.1$, and the value of m is determined depending on the situation. The pressure ratio p_F/p_R is determined so that the flow speed v_F at inlet ($X_1 = -L_-$ in channel F) satisfies $v_F/c_R = 2 \times 10^{-3}$, where $c_R = (2\kappa T_R/m^A)^{1/2}$ is the reference thermal velocity of A-molecules. Another parameter is the value of pressure drop p_D/p_R , which determines the flux through the membrane Q^α . In the case of $T_F/T_R = 1.1$, it is possible to use (2.1) to determine the value of p_D/p_R . For other cases, $T_F/T_R = 1$ and 0.9 , the solutions are parameterized by p_D/p_R .

Figure 2.7 shows the distribution of mole percentage χ of smaller molecules A [panel (a)] and average flow velocity v of the mixture [panel (b)] in channel F along X_1 axis. The values of χ and $|v|$ in channel R are very close to those in F. The number of micro-channels $m = 8 \times 10^4$ for $T_F/T_R = 1, 1.1$ and $m = 2 \times 10^2$ for $T_F/T_R = 0.9$. The solutions depend on p_D/p_R for $T_F/T_R \leq 1$, and thus two extreme cases are shown in the figure. As is expected in section 2.2.1, for the case of $T_F/T_R = 1.1$, the mole percentage χ increases with X_1 while the flow velocity v is almost constant, which allow us to extend the membrane and thus enlarge the variation of the mole percentage. Conversely, the value of χ decreases with X_1 for $T_F/T_R \leq 1$. The amount of decrease gets larger as pressure drop p_D/p_R increases, since the molecular flow through the membrane increases. However, large molecular flow through the membrane leads to

small downstream flow speed in channel F. There is an upper limit for the value of p_D/p_R , where the flow velocity v vanishes at $X_1 = L + L_+$. This state is shown by label “max” in figure 2.7. The flow velocity v also drops for any intermediate values of p_D/p_R . Since it is impossible to extend the membrane to obtain larger variation of χ , $T_F/T_R \leq 1$ is not acceptable in the present device. The performance of the case with $T_F/T_R = 1$, which corresponds the membrane gas separator with Knudsen diffusion, is limited: both of the variation of mole percentage and the gas flow at U-bend part may remain small. This low performance explains why other mechanisms, such as solution diffusion [23–25], are applied in the main stream of the membrane gas separation. The case with $T_F/T_R > 1$ is promising since there is appreciable variation of mole percentage, and the flow does not vanish at U-bend part. In this case, the membrane can be extended to obtain larger variation of χ . Indeed other numerical simulations with larger number of micro-channels $m = 5 \times 10^5$ show larger variation of χ : the result for $\chi_I = 0.1\%$ is $\chi_I + \Delta\chi = 12.5\%$, for $\chi_I = 10\%$ is $\chi_I + \Delta\chi = 96\%$, and for $\chi_I = 95\%$ is $\chi_I + \Delta\chi = 99.98\%$. Since the membrane can be extended as a result of the molecular exchange condition (2.1), it seems possible to realize as large variation of mole fraction as desired using the presented idea.

In view of these results, the experiments are carried out for $T_F/T_R > 1$. That is, the heated part H (unheated part C) of the fabricated device shown in section 2.2.2 corresponds to channel F (channel R) in section 2.2.1.

Before proceeding further, I have to discuss the molecular model for gas mixtures. The present model – hard-sphere molecules with the same diameter – is so simple that a quantitative disagreement is caused between the theoretical and experimental results. Instead, the basic concept in section 2.2.1 of the gas separation, which is based on the difference of the masses of gas molecules for any gas mixture, is well embodied by this simple model. The effect of realistic model can be confirmed by separate numerical simulation for specific gas mixture. It is easy to carry out the test since database [13] provides the data for various intermolecular potentials, just in the same formulation proposed in [11, 12]. For Lennard-Jones (LJ) model of Ne-Ar mixture ($m^B/m^A \approx 2.0$) at $T_F = 330$ K, $T_R = 300$ K, $m = 5 \times 10^4$, $t/d = 100$, $D/d = 500$, $\chi_I = 50\%$, $\text{Kn} = 0.5$ and $v_F/c_R \approx 2.1 \times 10^{-3}$, the value of $\Delta\chi$ is around 25 %, while the corresponding hard-sphere (HS) result with $m^B/m^A = 2$ and $d_m^A = d_m^B$ is $\Delta\chi \approx 27\%$. Except the value of $\Delta\chi$, there are various quantitative differences between LJ and HS results. For example, the value of pressure drop p_D/p_R is $p_D/p_R = 0.012$ for LJ and 0.005 for HS, the net volume flux Q^A through the micro channels for HS is almost twice of that for LJ. However, it is clear that HS model gives qualitatively the same result with realistic LJ model. I choose simpler HS model for the present 2D simulation, which aims to estimate the qualitative feature of the fabricated device for various gas mixtures.

2.3.2 Performance simulation

Now the numerical simulation is carried out for the fabricated device described in section 2.2.2. The mass ratio is $m^B/m^A = 10$, which corresponds to the helium-argon

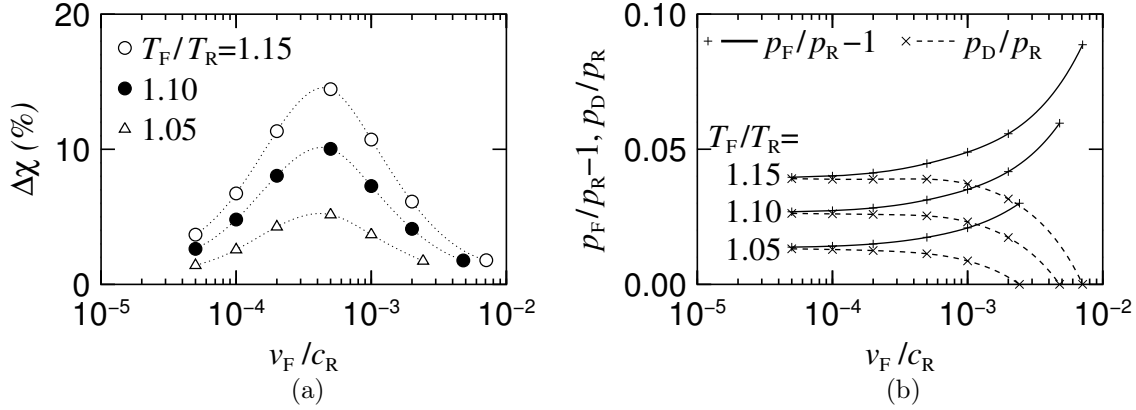


Figure 2.8: Result of numerical simulation for the fabricated device. Effects of the flow speed v_F/c_R and the temperature ratio T_F/T_R . $m^B/m^A = 10$, $\text{Kn} = 2$, $t/d = 10^3$, $D/d = 2 \times 10^3$, and $L/d = 3 \times 10^5$. (a) the gain of mole percentage $\Delta\chi$, and (b) the pressure ratio $p_F/p_R - 1$ and the pressure drop p_D/p_R versus v_F/c_R . The results for $T_F/T_R = 1.05, 1.1, 1.15$.

mixture used in the experiments in the next section. According to the product specification of the MCE membrane and the mean free path of helium molecules at atmospheric pressure, the parameters are set as follows: $\text{Kn} = 2$, $t/d = 10^3$, $D/d = 2 \times 10^3$, $m = 1.5 \times 10^5$, and $\chi_1 = 50$ %. The molecular model is the HS model with the same diameter of molecules.

Firstly I analyze the effect of the flow speed over the membrane, since the present device depends on the convection in channel F and R. If there were no convection effects, the outflows of the micro-channels in F and R may diffuse upstream and downstream without distinction. Figure 2.8(a) shows the gain of mole percentage $\Delta\chi$ for various values of v_F/c_R . The results are shown for $T_F/T_R = 1.05, 1.1, 1.15$. It is clear that $\Delta\chi$ becomes smaller for smaller values of v_F/c_R . Smaller v_F/c_R leads to larger diffusion in channels F and R, and this causes larger difference of χ between channels R and F at the same X_1 . Then the molecular exchange flow through the micro-channels is choked by the diffusion in micro-channels. For larger values of v_F/c_R , the effect of molecular exchange flow is diluted by larger fluxes in channels F and R, which results in smaller gain of mole percentage. As a result, $\Delta\chi$ is maximized at an intermediate value of v_F/c_R . Its value is $v_F/c_R \approx 0.05$, which corresponds to $v_F \approx 60$ cm/s for helium-argon mixture. It is noted that the molecular exchange flow does not vanish for larger values of v_F/c_R ; the numerical data shows that the values of $Q^A (= -Q^B)$ increase and approach some upper bounds as v_F/c_R increases. There is, however, an upper limit for v_F/c_R , since larger flow speed induces larger pressure drop along channels F and R. The values of pressure ratios p_F/p_R and p_D/p_R are shown in figure 2.8(b) versus v_F/c_R . For larger values of v_F/c_R , the values of p_F/p_R increase to establish the prescribed flow speed. This leads to smaller values of p_D/p_R in order to establish molecular exchange state (2.1). That is, $p_D = 0$ gives the upper limit of v_F/c_R . While the solution does not exist

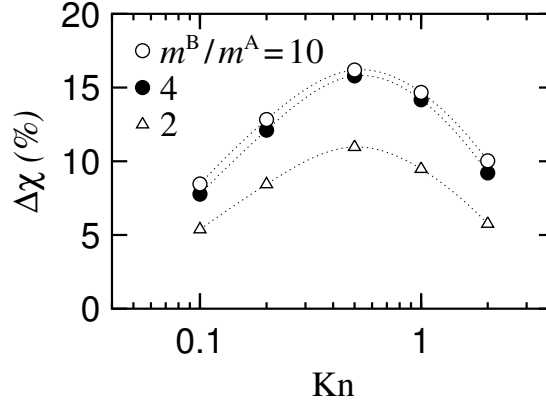


Figure 2.9: The numerical results of the gain of mole percentage. Effect of the Knudsen number Kn and mass ratio m^B/m^A . $T_F/T_R = 1.1$, $v_F/c_R = 5 \times 10^{-4}$, $t/d = 10^3$, $D/d = 2 \times 10^3$, and $L/d = 3 \times 10^5$.

for larger values of v_F/c_R depending on T_F/T_R , the value of $\Delta\chi$ shows almost linear dependence on $T_F/T_R - 1$ around $v_F/c_R \approx 10^{-3}$. This relation will be confirmed in the experiment in section 2.4.3.

The performance simulation is also carried out for various values of Knudsen number Kn and mass ratio m^B/m^A . The values of $\Delta\chi$ versus Kn are plotted for $m^B/m^A = 2$, 4, and 10. The temperature ratio $T_F/T_R = 1.1$ and flow speed is $v_F/c_R = 5 \times 10^{-4}$. The values of other parameters are the same as those used in figure 2.8. The values of $\Delta\chi$ is maximized at $Kn \approx 0.5$ for any value of m^B/m^A . The maximum at intermediate Kn corresponds to the feature of the molecular exchange flow (cf. section 2.2.1) through the micro-channels. In the continuum limit $Kn \rightarrow 0$, the thermal transpiration thus the molecular exchange vanishes. In Knudsen limit $Kn \rightarrow \infty$, the speed ratio of A-gas to B-gas is $\sqrt{m^B/m^A}$ for both Poiseuille and thermal transpiration flows. Since the speed ratio is $\sqrt{m^B/m^A}$ for any linear combination of these flows in this case, the molecular exchange is impossible. As the result, the size of molecular exchange flow is maximized at an intermediate Knudsen number [19]. It is noted that $\Delta\chi$ for $m^B/m^A = 4$ and 10 are almost the same. As is discussed above, the speed of molecular exchange flow is determined by the difference of the species-dependency of Poiseuille and thermal transpiration flows at intermediate Knudsen numbers. Therefore, it is natural that the dependence of the speed of molecular exchange flow on m^B/m^A is complicated.

2.4 Experimental results

2.4.1 Performance Test Setup

The measurement apparatus is shown in figure 2.10. The gas mixture is fed to inlet H_1 of the test device. The outlet H_2 is connected to inlet C_1 via a needle valve V_1 .

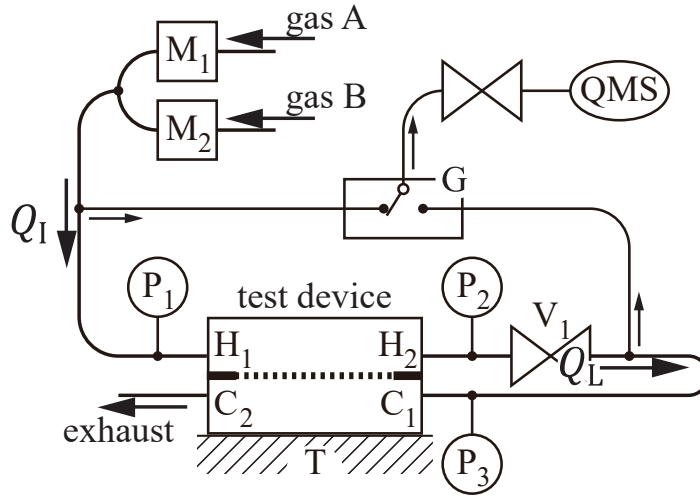


Figure 2.10: Diagram of measurement system.

The outlet C_2 is open to atmospheric environment. The volume flux of the feeding is denoted by Q_I , and that of the loop part $H_2 \rightarrow C_1$ by Q_L . Q_I is controlled by two mass flow controllers M_1 [Horiba STEC SEC-400 (FS 100 sccm)] and M_2 [Horiba STEC SEC-400 (FS 50 sccm or 1000 sccm, depending on the size of Q_I)]. The volume flux at the loop part $H_2 \rightarrow C_1$, Q_L , is controlled by V_1 , which may be Swagelok SS-SS1 or SS-2MG depending on the size of Q_L . The valve V_1 is replaced by a tube for several cases with large value of Q_L , and the flux is controlled by the length of the tubing. All part of these connections are done by the stainless tube with inner diameter 1 mm. Three differential pressure sensors [Honeywell ASDXRRX010NGAA5 (FS 2.5 kPa) or Freescale Semiconductor MPX2053 (FS 50 kPa)] P_1 , P_2 , and P_3 are connected, respectively, around H_1 , H_2 , and C_1 to obtain the differential pressure from the environment. The pressure measured by sensor P_i will be denoted by p_i ($i = 1, 2, 3$). The symbol G in the figure is a two-port gas sampling system, which can take small amount of sample gas intermittently from desired port without mixing the gases at two ports. One port is connected to H_1 , and the other port is connected to C_1 . The sampled gas is lead to QMS (quadrupole mass spectrometer, Pfeiffer QMS200) with a metal dosing valve (Pfeiffer UDV040) to analyze the component of the sampled gas. The device is put on a thermostat table T to keep the temperature T_C of plate C of the test device at 300 K.

It is noted that the available range of Q_L depends on the temperature difference $\Delta T = T_H - T_C$. In the isothermal case $\Delta T = 0$, Q_L is smaller than Q_I , since some part of the feed gas flows from H_1 to C_1 through the membrane and does not reach H_2 . In other cases, $\Delta T > 0$, the thermal transpiration flow in the direction $C \rightarrow H$ expands the available range of Q_L . The value of Q_L is expressed by Q_I and Q^α introduced in section 2.2.1 as follows:

$$Q_L = Q_I + Q^A + Q^B.$$

In order to establish the pure molecular exchange state (2.1), the condition

$$Q_L = Q_I \quad (2.5)$$

is met in the experiment by controlling the opening V of valve V_1 as follows: (i) Remove the test device and connect $H_1 \rightarrow H_2$ and $C_1 \rightarrow C_2$ by straight pipes to allow Q_L to specified using M_1 and M_2 . (ii) Measure the pressure drop $\Delta p = p_2 - p_3$ by valve V_1 for various valve openings V and volume flux Q_L to construct a calibration function h_C as

$$\Delta p = h_C(V, Q_L), \quad (2.6)$$

which can be used independent of the existence of the test device. In the main experiment, the pressure difference Δp are determined by V , Q_I , and ΔT :

$$\Delta p = \Delta p(V, Q_I, \Delta T). \quad (2.7)$$

Then the valve openings V is determined by (2.5)–(2.7) for prescribed values of Q_I and ΔT .

2.4.2 Knudsen pump performance

First of all, I have to confirm that the thermal transpiration flow through the membrane is successfully induced by the present device. To this end I shut the valve V_1 to force the entire supplied gas to go through the membrane. Then, the experiment is carried out as follows: (i) The heater of the test device is turned on, and controlled to keep a constant temperature difference ΔT ; (ii) Supply gas mixture through M_1 and M_2 at volume flow rate Q_I ; (iii) Measure the pressure difference Δp for various flow rates Q_I . The results for negative values of Q_I are obtained by connecting gas supply from M_1 and M_2 to C_2 of the device with H_1 being open to the atmosphere.

The experiment is carried out for 50% v/v mixture of helium and argon, $\Delta T = 0, 20, 30$, and 45 K. The values of electricity supplied to the heater are, respectively, 1.6 W($\Delta T = 0$ K), 10.0 W(20 K), 14.1 W(30 K), and 20.0 W(45 K). The electricity does not vanish at $\Delta T = 0$ K since the environmental temperature is 286 K on average, which is lower than $T_C = 300$ K. The value of Δp is plotted versus Q_I in figure 2.11. At $\Delta T = 0$, the pressure difference Δp is almost proportional to the volume flux Q_I through the device. Their relation is represented by

$$Q_I(\text{sccm}) \approx 81\Delta p \text{ (kPa)} \quad (\Delta T = 0). \quad (2.8)$$

This is natural since the membrane has its own pressure drop. As ΔT increases, the relation is shifted; the gas flows from C part to H part ($Q_I < 0$) for $\Delta p = 0$ and the pressure at H part is higher than that at C part ($\Delta p > 0$) when the gas flow vanishes ($Q_I = 0$). This is the effect of the thermal transpiration, and the device works as a Knudsen pump in the same way as in [17]. Incidentally the effect of larger viscosity for higher temperature is seen in the figure; $dQ_I/d\Delta p \approx 70$ for $\Delta T = 45$ K. The value of Δp

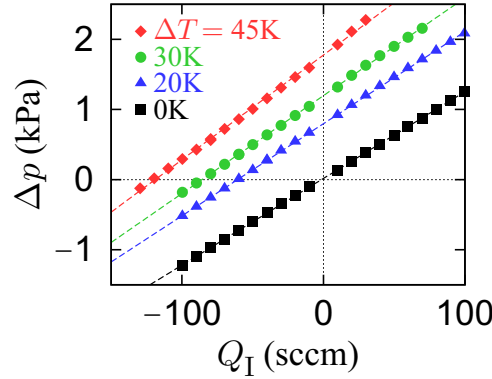


Figure 2.11: Knudsen pump performance. Δp vs Q_I for various ΔT . The data for 50 %v/v mixture of helium and argon, $T_C = 300$ K and atmospheric pressure at the outlet. The symbols represent the result of experiments. $\Delta T = 0$: black square, 20 K: blue triangle, 30 K: green circle, and 45 K: red diamond. The linear regressions are also shown in the figure.

at $Q_I = 0$ is the maximum pressure difference obtained by the thermal transpiration. These values are $\Delta p = 0.80$ kPa ($\Delta T = 20$ K), 1.20 kPa (30 K), and 1.78 kPa (45 K). These results are close to the result shown in [17]. Q_I at $\Delta p = 0$ is the maximum volume flux obtained by the thermal transpiration. Their values are 61 sccm ($\Delta T = 20$ K), 86 sccm (30 K), and 119 sccm (45 K). The value of flux Q_I at $\Delta p = 0$ is roughly proportional to ΔT , and is expressed by

$$Q_I \text{ (sccm)} \approx -2.8\Delta T \text{ (K)} \quad (\Delta p = 0) \quad (2.9)$$

The value of volume flux at $\Delta T = 30$ K is about 90 times larger than those given in [17], since the size of the membrane in the present device is about 10 times larger and the sound speed is higher with helium molecules. These results show that the present device successfully induces the thermal transpiration flow.

Now I describe the main experiment of gas separation for two types of gas mixtures: (I): helium-argon 50 % v/v mixture and (II): helium-neon 50 % v/v mixture. The process of the experiment is as follows: (i) Keep the prescribed temperature difference ΔT with the heater; (ii) Supply the gas mixture of volume flux Q_I to the device; (iii) Set the volume flux at loop part Q_L identical to Q_I with the valve V_1 ; (iv) Analyze the components of the gas at H_1 and C_1 . The detailed process of (iv) is as follows: (iv.1) Sample the gas from H_1 , and analyze the gas components by QMS; (iv.2) The same analysis is performed for C_1 ; (iv.3) Repeat (iv.1) –(iv.2) four times; (iv.4) Finally carry out process (iv.1) again. Thus I obtain five mole percentages $\chi[H_1^{(n)}]$ ($n = 1, 2, \dots, 5$) at H_1 , and four $\chi[C_1^{(n)}]$ at C_1 , where χ is the mole percentage of helium. In each QMS analysis, sampling was repeated 25 times with 3 minutes interval, then first 15 data are discarded to avoid the effect of the residual gas in the tubing, and the average of

remaining 10 is adopted as the final result. I can calculate the difference of mole percentages obtained by the test device $\Delta\chi^{(n)}$ ($n = 1, 2, \dots, 4$), which corresponds $\chi_L - \chi_F$ in the numerical simulation in section 2.3, by

$$\Delta\chi^{(n)} = \chi \left[C_1^{(n)} \right] - \frac{\chi \left[H_1^{(n+1)} \right] + \chi \left[H_1^{(n)} \right]}{2}. \quad (2.10)$$

It is noted that the restriction (2.5) is achieved only approximately. It takes several hours to carry out process (iv) above, and I observe some deflection of p_i due to the variations of environmental temperature and pressure during this period. In the case with large volume flux Q_I , a pressure sensor with larger full scale is used to measure large pressure variation along the flow channels. When Q_L is controlled by the length of the tubing, it is very difficult to select a tubing which precisely satisfies $Q_L \approx Q_I$. Therefore, in the following results, the average volume flux Q defined by

$$Q = \frac{Q_I + Q_L}{2},$$

is used instead of Q_I .

2.4.3 Gas separator performance

The results of the experiments are shown in figures 2.12–2.15. Figure 2.12 shows the values of $\Delta\chi$ [average of four $\Delta\chi^{(n)}$ in (2.10)] versus Q . Figure 2.12(a) shows the result of experiment (I), where the range of volume flux Q is limited but the experiments are carried out for several temperature differences $\Delta T = 20, 30$, and 45 K. The result for experiment (II) is shown in figure 2.12(b), where ΔT is fixed to 30 K and the experiments are carried out for a wider range of Q . In both cases, the value of $\Delta\chi$ is positive; that is, the smaller gas – helium – is concentrated at the loop part $H_2 \rightarrow C_1$ as is anticipated by the numerical simulation in section 2.3. In experiment (I), the value of $\Delta\chi$ for a fixed value of Q increases linearly as ΔT increases. The value of $\Delta\chi$ for given ΔT also increases as Q increases. The value of $\Delta\chi$ reaches 15 % for the case of $\Delta T = 45$ K and $Q = 40$ sccm. In experiment (II), the value of $\Delta\chi$ is maximized around $Q = 100$ sccm. Since the volumetric porosity of the copper mesh [see figure 2.5(b)] is around 60 %, the flow velocity along the membrane is around 0.5 m/sec at $Q = 100$ sccm. These qualitative features of $\Delta\chi$ match the results of the numerical simulation in section 2.3. The values of $\Delta\chi$ is much larger than the variance in four measured values of $\Delta\chi^{(n)}$; the value of $\max \Delta\chi^{(n)} - \min \Delta\chi^{(n)}$ for each experiment is 0.09 % on average. The errors in Q result from the accuracy of the mass flow controllers M_1 and M_2 , and their total error is smaller than 3.3 sccm for $Q \leq 100$ sccm and 29 sccm for $Q > 100$ sccm.

Figure 2.13 shows the difference of Q_I and Q_L in percentage:

$$Err_Q = 100 \frac{Q_I - Q_L}{Q}.$$

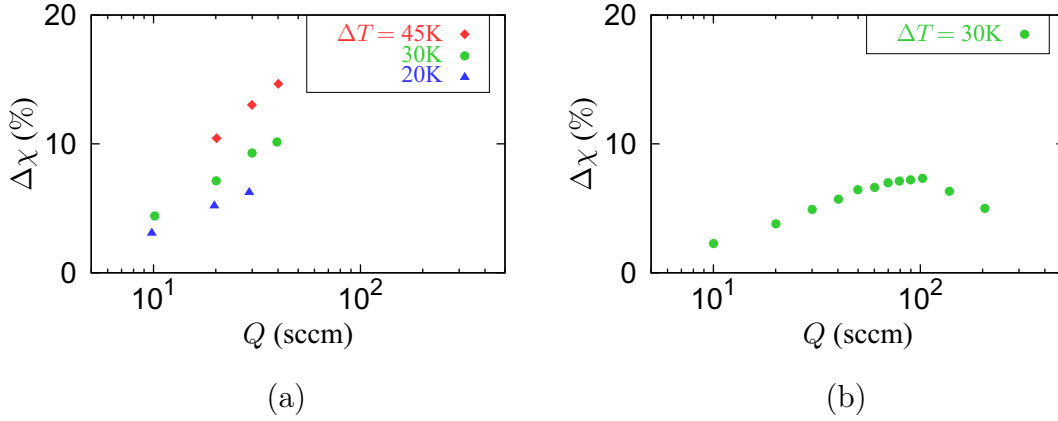


Figure 2.12: Gas separation performance I: $\Delta\chi$ vs Q . (a) Experiment (I) helium-argon mixture, $\Delta T = 20, 30$, and 45 K; (b) experiment (II) helium-neon mixture, $\Delta T = 30$ K.

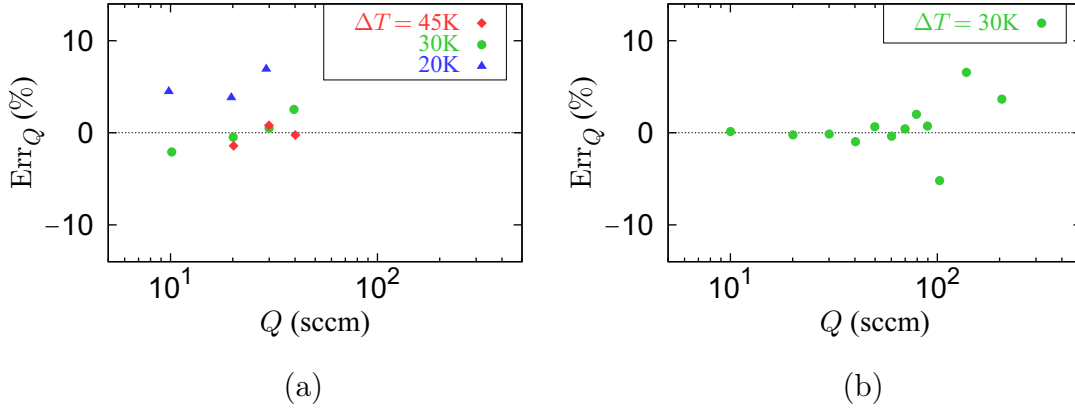


Figure 2.13: Gas separation performance II: The value of $\text{Err}_Q = 100(Q_I - Q_L)/Q$ vs Q . (a) Experiment (I) helium-argon, $\Delta T = 20, 30$, and 45 K; (b) experiment (II) helium-neon, $\Delta T = 30$ K.

The experiments for $Q \leq 40$ sccm are carried out by smaller valve V_1 (SS-SS1), those with $40 \text{ sccm} < Q \leq 100$ sccm are carried out by larger valve (SS-2MG). The experiments are carried out without valve V_1 for larger values of Q . As is shown in the figure, the maximum size of the error is around 7 %. In order to confirm that the molecular exchange $Q^A > 0$ and $Q^B < 0$ occurs in the device, Q^A and Q^B are calculated by

$$\begin{aligned} Q^A &= \chi[C_1] Q_L - \chi[H_1] Q_I, \\ Q^B &= (1 - \chi[C_1]) Q_L - (1 - \chi[H_1]) Q_I. \end{aligned}$$

The results are plotted in figure 2.14. It is clear that helium flows in the direction of $C \rightarrow H$ through the membrane, while argon or neon flows in the direction of $H \rightarrow C$. The value of $Q^A - Q^B$ increases as Q increases in the region studied.

Figure 2.15 shows the result of the pressure in these experiments. Since the pressure

drops significantly along the tubings for larger values of Q , the measured values of the pressures depend much on where to connect the sensors. The pressure can be estimated at each trench shown in figure 2.4(b) from the values of p_i , Q_I , and Q_L , assuming Hagen-Poiseuille flow in the tubing. The differences of the estimated pressures are shown in figure 2.15, where the pressure difference between the trenches next to H_1 and C_2 ports is denoted by Δp_I and that next to H_2 and C_1 ports by Δp_L . The values of Δp_I and Δp_L in experiment (I) are around 1 kPa for $\Delta T = 30$ K, and it is comparable to the pressure difference $p_F - p_R$ expected by numerical simulation for $m^B/m^A = 10$ and $T_F/T_R = 1.05$ [see figure 2.8(b)]. The pressure differences Δp_I is close to Δp_L in experiment (I) where Q is relatively small, while Δp_I is fairly larger than Δp_L in experiment (II) for the larger flow rate Q . Their large difference, i.e., large pressure gradient along the membrane, means that the molecular exchange condition (2.1) is satisfied as an average over the membrane and is not satisfied locally for each micro-channel.

2.5 Discussion

The performance of the device has been analyzed numerically in section 2.3 and experimentally in section 2.4. It is clear that the results in the preceding two sections are qualitatively in a good agreement with each other. The fabricated device, however, naturally has various indeterminateness. In this section, some of them will be discussed with quantitative comparisons of the results.

As for the thermal transpiration performance, the actual temperature difference applied to the MCE membrane is smaller than the temperature difference between the metal plates H and C. The exact properties of the membrane itself are also unknown: the actual size of pores are unknown because it is an ordinary filter product; the effective porosity may be affected by the metal meshes covering the surfaces of the membrane. These factors can be estimated from the pressure-flux relation obtained in section 2.4.2. Let $\theta\Delta T$ be the temperature difference applied to the membrane and d_{MCE} and ε be, respectively, the effective pore diameter and porosity of the membrane. From the linear theory of the Boltzmann equation [cf. equation (A.2) in appendix A], the volume flux $Q^* = Q^A + Q^B$ through the device is given by

$$Q^* = S\varepsilon \frac{d_{\text{MCE}}}{t} \sqrt{\frac{2\kappa T_C}{m^A}} \left[\frac{\theta\Delta T}{T_C} N_T + \frac{\Delta p}{p_C} N_p \right], \quad (2.11)$$

where S and t are, respectively, the area and thickness of the MCE membrane, p_C is the reference pressure (pressure at C_2), and N_* ($*$ = T , p) are nondimensional functions of Knudsen number ℓ_C/d_{MCE} (ℓ_C : reference mean free path of A-molecules at number density $p_C/\kappa T_C$ of molecules). The values of N_* also depend on gas components, molecular model, and the shape of the cross section of micro-channel. For binary mixtures of hard sphere molecules, enough amount of data is available only for 2D channel [13]. On the other hand, for pure gases, detailed data for various cross sectional shapes including 3D

channels are available for BGK and S-model [1, 9], and they are used in the following discussion. From the present experimental conditions, $T_C = 300$ K, $p_C = 101$ kPa, and $S = 9.0$ cm². For binary mixture of hard sphere molecules,

$$\sqrt{\frac{2\kappa T_C}{m^A}} = 1120 \text{ m/s}, \quad \ell_C = 1.70 \times 10^{-7} \text{ m}, \quad m^B/m^A = 10, \quad \chi = 50 \% \quad (2.12)$$

are adopted here to express the 50% v/v helium-argon mixture used in the experiments. For BGK and S-model of pure gas, appropriate values of (m^A, ℓ_C) , or $(m^{\text{BGK}}, \ell^{\text{BGK}})$, have to be determined for the present gas mixture. Since the behavior of the gas at intermediate Knudsen numbers is important in the present device, Knudsen minimum is used to determine the parameters (namely the value of $|N_p|$ takes its minimum value at some intermediate Knudsen number). The adopted parameters are

$$\sqrt{\frac{2\kappa T_C}{m^{\text{BGK}}}} = 623 \text{ m/s}, \quad \ell^{\text{BGK}} = 3.71 \times 10^{-7} \text{ m}, \quad (2.13)$$

for BGK model and

$$\sqrt{\frac{2\kappa T_C}{m^S}} = 619 \text{ m/s}, \quad \ell^S = 2.90 \times 10^{-7} \text{ m}, \quad (2.14)$$

for S-model so that these models give the same volume flux Q^* and diameter d_{MCE} with the binary mixture of hard sphere gas ($m^B/m^A = 10$ and $\chi = 50$ %) at Knudsen minimum for 2D channel.

Since the values for N_T and N_p are available, the results of experiment (2.8) and (2.9) give the relation among θ , d_{MCE} , and ε . That is, the ratio of two volume fluxes under $\Delta p = 0$ and $\Delta T = 0$ is given by, from (2.11),

$$\theta \frac{N_T}{N_p} = \frac{Q(\Delta p = 0)}{Q(\Delta T = 0)} \frac{\Delta p/p_C}{\Delta T/T_C}.$$

This equation with the results (2.8) and (2.9) determines the value of the Knudsen number or the value of d_{MCE} as a function of θ . The value of ε is then obtained from (2.8) and (2.11). The result is shown in figure 2.16. The panel (a) shows the effective pore diameter d_{MCE} versus the effective porosity ε of the MCE membrane, and panel (b) shows the temperature difference ratio θ versus ε . The black lines are obtained by using N_T and N_p for 2D channel with binary mixture of hard sphere molecules of $m^B/m^A = 10$ and mole percentage 50%. The red lines and green symbols [which are almost on the black line in panel (a)] are those with 2D channel results with, respectively, BGK and S-model for pure gas. The blue symbols are also the result of BGK model but 3D channel shape (square cross section). The similar result for S-model is also shown in the figure by orange symbols. As the result of conversion (2.13) and (2.14), BGK and S-model give almost the same results of $(\varepsilon, d_{\text{MCE}})$ relation with the binary mixture of hard sphere molecules for 2D case. On the other hand, the difference between 2D and

3D channel is appreciable. Assuming that the conversions (2.13) and (2.14) are still valid for 3D model, the results of experiments are discussed using $(\varepsilon, d_{\text{MCE}}, \theta)$ relation for 3D models. Since the porosity of MCE membrane, stainless fiber sheet, and copper mesh are, respectively, 0.65, 0.8, and 0.6, the effective porosity ε will be in the range of $0.3 \lesssim \varepsilon \lesssim 0.65$. Therefore, the effective pore size d_{MCE} is in the range

$$0.1 \mu\text{m} \lesssim d_{\text{MCE}} \lesssim 0.2 \mu\text{m}, \quad (2.15)$$

from the result for 3D case in figure 2.16(a). This is consistent with the product specifications of the MCE membrane (pore size $0.1 \mu\text{m}$). The above result shows a slightly larger pore size, which can be caused by the complicated structures of the membrane. The value of θ , which is obtained by 3D data, shows some model dependency but is around

$$\theta \approx 0.3,$$

which means that only 30 % of the temperature difference ΔT is conducted to the MCE membrane. This is close to the corresponding value in [17], where around 20 % of the temperature difference between hot and cold parts is conducted to the MCE membrane. The heat conduction can be prevented by the flow channels F and R of height 0.2 mm along the MCE membrane.

Now I discuss the results for gas separation experiment described in section 2.4.3. The gain $\Delta\chi$ of helium in experiment (I), figure 2.12(a), corresponds to the result of numerical simulation $\Delta\chi$ in figure 2.8(a). The comparison is done by matching the temperature difference and the pore size of the membrane. Since the temperature difference regarding to the MCE membrane may be $\theta\Delta T$, the corresponding value of the temperature ratio in the numerical simulation is $T_{\text{F}}/T_{\text{R}} = 1 + \theta\Delta T/T_{\text{C}}$. That is, $T_{\text{F}}/T_{\text{R}} - 1 \approx 0.02$ ($\Delta T = 20$ K), 0.03 ($\Delta T = 30$ K), and 0.05 ($\Delta T = 45$ K). The values of $\Delta\chi$ for these $T_{\text{F}}/T_{\text{R}}$ can be estimated from the results in figure 2.8 since $\Delta\chi$ is almost linear to $T_{\text{F}}/T_{\text{R}} - 1$ for smaller values of $v_{\text{F}}/c_{\text{R}}$; e.g., $\Delta\chi \approx 3$ % for $T_{\text{F}}/T_{\text{R}} = 1.03$ and $\Delta\chi \approx 5$ % for $T_{\text{F}}/T_{\text{R}} = 1.05$. The matching of pore size (2.15) is complicated, since it is related to the device sizing parameters, D/d , L/d , and t/d as well as the Knudsen number. The parameters used in figure 2.8 match the fabricated device if $d_{\text{MCE}} = 0.1 \mu\text{m}$; in this case the numerical data corresponds to the device with $D = 0.2$ mm, $L = 30$ mm, $t = 100 \mu\text{m}$, and $\text{Kn} = 2$. In the case of $d_{\text{MCE}} = 0.2 \mu\text{m}$, the values of D , L , and t are doubled and $\text{Kn} = 1$. The larger D and t may decrease the gain $\Delta\chi$ of the numerical results, and the larger L may increase it. Assuming linear dependency of $\Delta\chi$ on $1/D$, $1/t$ and L , the performance of the fabricated device may be twice of the numerical data in figure 2.8 except the effect of the Knudsen number. The effect of Knudsen number can be estimated from figure 2.9; the gain for $\text{Kn} = 1$ may be around 1.5 times larger than that for $\text{Kn} = 2$.

According to above discussion on temperature difference and pore size, the maximum gain $\Delta\chi$ in experiment (I) at $\Delta T = 45$ K is estimated to be in the range of 5 % ($d_{\text{MCE}} = 0.1 \mu\text{m}$) and 15 % ($d_{\text{MCE}} = 0.2 \mu\text{m}$) from the results of numerical simulation. Figure 2.9 also shows that the gain $\Delta\chi$ is almost the same for $m^{\text{B}}/m^{\text{A}} = 4$ and 10.

Therefore, the gain $\Delta\chi$ in experiment (II), where $\Delta T = 30$ K, is estimated to be in the range from 3 % to 9 %. In the experiment (I), as seen from section 2.4.3, the value of $\Delta\chi$ already marks 15 % for $\Delta T = 45$ K, and larger value of $\Delta\chi$ is expected for larger flux Q , while the maximum gain for experiment (II) is 7 %. It is clear that the $\Delta\chi$ obtained in the experiment is too large only for helium-argon mixture.

There will be many reasons for this disagreement. The 2D shape of micro-channel used in the numerical simulation and the difference of effective porosity of the membrane do not explain the disagreement, since they are common to experiments (I) and (II). One of the possible reason is the selection of diameter of the molecules $d_m^A = d_m^B$ in the present numerical simulation. Since the ratio of the diameters of molecules calculated from the viscous coefficients are $d_m^{\text{Ar}}/d_m^{\text{He}} \approx 1.7$ and $d_m^{\text{Ne}}/d_m^{\text{He}} \approx 1.2$ [1], the argon or neon molecules experiences more collisions than expected in the simulation. That is, the effective Knudsen number for the experiment is much smaller than $\text{Kn} = 1$ or 2, and this results in larger $\Delta\chi$ obtained in the experiment, especially for helium-argon experiment (I).

2.6 Conclusion

In section 2.2, I proposed a device that induces the molecular exchange flow through the membrane with the aid of the thermal transpiration. The device accumulates the molecular exchange effect as the gradient of the mole fraction along the membrane. The performance is estimated theoretically in section 2.3, where the combination of mass conservation and rarefied gas flow database [13] leads to plausible results. The performance of the fabricated device is tested in section 2.4. The results of experiments are in qualitatively good agreement with the theoretical results. That is, the gas component of smaller mass of molecules is concentrated at the loop part between heated and unheated side of the membrane, the gain of mole percentage $\Delta\chi$ is almost proportional to the temperature difference, and $\Delta\chi$ takes its maximum value at some flow speed along the membrane. Furthermore, the quantitative features are also reproduced by the theoretical results. The characteristic values of the device, such as the maximum variation of mole percentage $\Delta\chi$, the appropriate flow speed along the membrane for obtaining large values of $\Delta\chi$, and the pressure difference between the front and rear side of the membrane Δp_I or Δp_L , remain in the same order with the corresponding values estimated by the theory in section 2.3.

The present device is somewhat similar to the membrane gas separator. Indeed the motion of molecules in the membrane is the key to the device, and some membrane gas separator make use of the counter flow arrangement as in the present device. However, the molecular transport through the membrane is quite different. In the membrane gas separator, both the molecules of product and residual gas flow in the same direction, and thus the selectivity is quite important. It is also difficult to obtain high purity output. In the present device, molecular exchange – the molecules of product and residual gas flow in the opposite direction – is established. This device is free from the

limitation of the selectivity [26], and no limit on the purity of the products is found in the numerical simulation. The molecular exchange setup enables us to use low cost membranes with larger pore size ($0.1 \mu\text{m}$) and thickness ($110 \mu\text{m}$) compared with those used in the membrane gas separation.

In view of the flow direction in the membrane, the present method can be considered as a revision of the thermal diffusion column method [43]. In the thermal diffusion column, the small molecules and large molecules flow in the opposite radial direction due to the temperature and pressure gradient, which is essentially the same as the molecular exchange flow. The difficulty in the thermal diffusion column comes from the principle that the effect of molecular exchange is accumulated by the natural convection induced in the longitudinal direction of the column. The natural convection is characteristic to the gas in the continuum limit while the molecular exchange flow is characteristic to rarefied or molecular gas [19]. In the present device, the properties of continuum flow are utilized too, but they are separated from the molecular exchange flow in the membrane. Therefore, local Knudsen number can be chosen separately in channel F and R and in the micro-channel.

The present device, however, does not produce concentrated gas. All of the concentrated gas, which flows out the front side of the membrane, flows back into the rear side of the membrane except small amount of sample gas taken by the gas sampling system. The problem is that the outlet of the residual gas is located close to the inlet for the feed gas (cf. figure 2.1); they are separated only by a single membrane which can maintain small difference of mole percentage. If the separator produces volume flux δQ_I of the gas with increment of mole percentage $\Delta\chi$ from volume flux Q_I of feed gas, the conservation of mass leads that the difference of mole percentage between the feed and residual is $\delta\Delta\chi/(1-\delta)$ without regard to the values of Q^A and Q^B through the membrane. This restricts the value of the production rate δ of present device. This limitation will be removed by more sophisticated constructions, e.g., the cascade connection of units or some reflux process of residual to arrange better positions of the inlet and outlet, which can be found in other methods of gas separation. The construction of such system is left for the future work. Another problem is the energy efficiency, which is not estimated in present work due to no product gas. In general, we cannot expect too much for the energy efficiency. The heated gas molecules may convey their energy in the random direction, and only a part of the energy is used to induce the thermal transpiration flow. The present device, however, works with small temperature differences around 30 K. Some pressure difference is also required, but it is as small as a few kilo pascals. It is important that the required pressure difference is the order of the pressure difference that can be induced by the thermal transpiration flow. Therefore, it is expected that this kind of device works with the energy supply of low level external heat, which would be quite unique compared with other methods of gas separation.

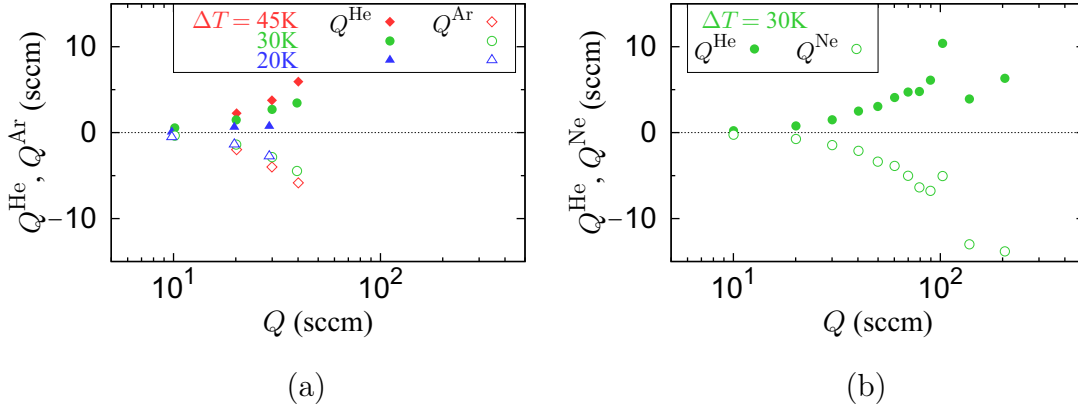


Figure 2.14: Gas separation performance III: The value of $Q^{\text{A}}, Q^{\text{B}}$ vs Q . (a) Experiment (I): A: helium, B: argon, $\Delta T = 20, 30$, and 45 K ; and (b) experiment (II): A: helium, B: neon, $\Delta T = 30\text{ K}$. The values of Q^{A} are shown by filled markers, and those of Q^{B} are shown by hollow markers.

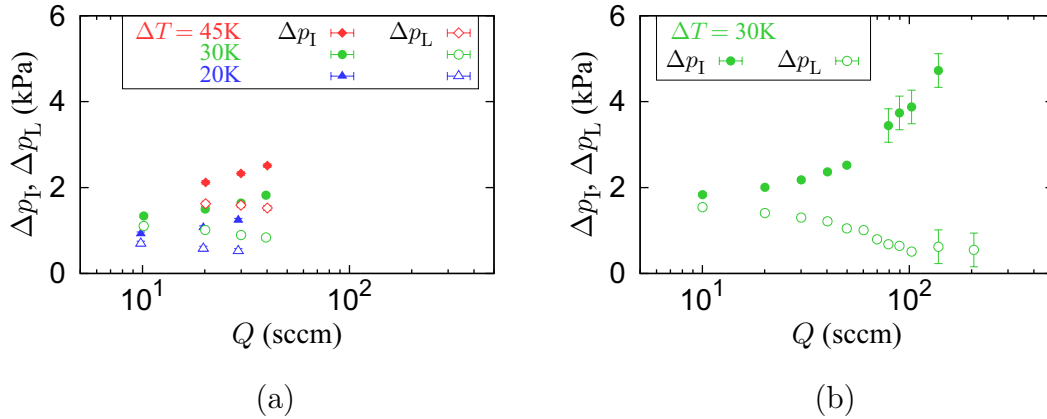


Figure 2.15: Gas separation performance IV: The pressure differences between membrane. Δp_{I} : filled markers, and Δp_{L} : hollow markers. (a) Experiment (I) helium-argon; (b) experiment (II) helium-neon. The error bar shows the standard deviation estimated from the precision of the pressure sensors used in each experiment.

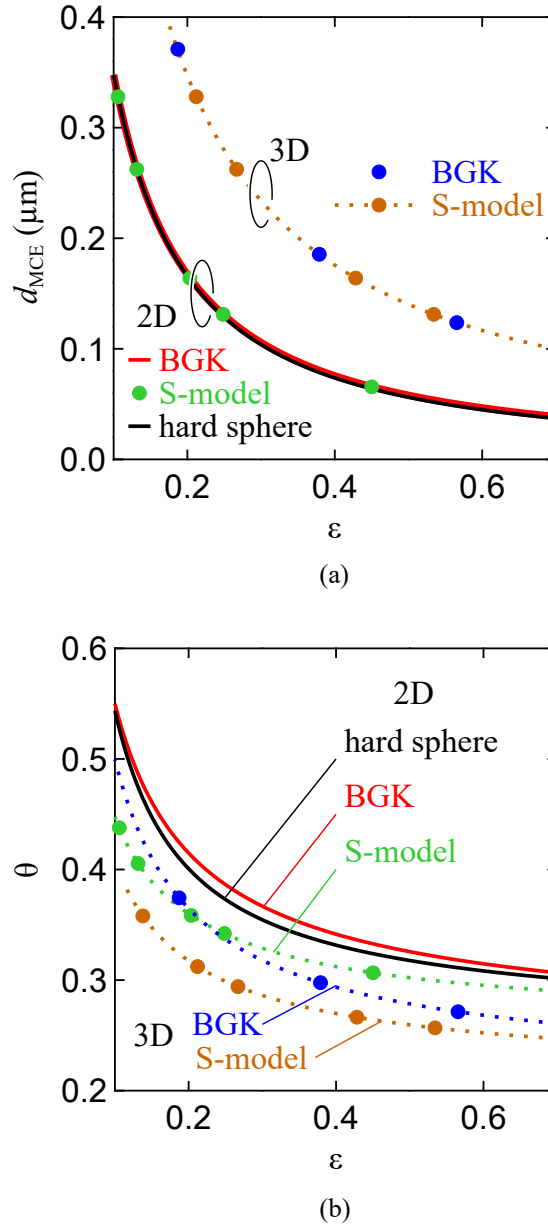


Figure 2.16: Estimated value of (a) temperature difference ratio θ and (b) effective pore diameter d_{MCE} versus effective porosity ε . The results with N_T , N_p for 2D channel and square channel (indicated by 3D in the figure). The black lines are the results with the binary mixture of hard sphere molecules (mass ratio 10 and mole percentage 50 %). The red lines and blue symbols are that with BGK model for pure gas. The green and orange symbols are that with S-model for pure gas. The dashed lines indicate the data by spline approximation.

Chapter 3

Simulation of Gas Separator

3.1 Introduction

Gas separation is one of the important technologies in various industrial processes, such as isolation and purification of gases in chemical plants, food processing, and semiconductor processes. Amongst various methods of separation, membrane gas separation is attractive for its simple device structure and high energy efficiency. Extensive research has been carried out on the fabrication of separation units and membranes with optimum macroscopic and microscopic structure [23, 24, 44]. The existing methods of membrane gas separation utilizes a property of pressure driven flow through membranes that the permeation speeds depend on gas species. However, because the pressure difference is the only driving force of the permeation, all component gases permeate in the same direction through membranes. This is the fundamental restriction of all conventional methods of membrane gas separation, and results in a difficulty in obtaining highly purified gases.

When the membrane is porous, a flow through a membrane can also be induced by a temperature gradient [27, 31]. This phenomena is called thermal transpiration [2], where a temperature gradient of a pore wall causes a motion of gases from the cold part to the hot part. Although the thermal transpiration is characteristic to the rarefied gas, it can be induced even at atmospheric pressure in microsystems, where their small feature dimensions can impose rarefied conditions without the need for vacuum.

In 2011, Gupta and Gianchandani [17] demonstrated thermal transpiration flow at atmospheric pressure by using a MCE membrane in their dime-sized Knudsen pump. According to this work, two driving forces are now available which can be controlled independently: pressure difference and temperature difference. Therefore, we can control two of the permeation speeds of component gases; it is possible to induce a flow where some component gas flows in the opposite direction to another. This flow is referred to as the molecular exchange flow, and it is numerically [35] and experimentally [45] shown that the molecular exchange flow is realized by a specific combination of the thermal transpiration and the pressure driven flow. I utilizes this flow to induce a concentration variation, and to remove the fundamental restriction of the conventional membrane

separation: all component gases permeate in the same direction.

The native gas separation effect of a small portion of a membrane, however, is too small for engineering purposes, because we cannot enlarge temperature difference in polymer membranes like the ones made of MCE. Therefore, in order to accumulate the separation effect of the molecular exchange flow, I adopt a counter flow setup similar to the hollow fiber membrane gas separation unit [23]. The counter flow setup is shown to be capable of accumulating the effects and inducing a significantly large concentration variation [45].

In the present work, I propose a design of membrane gas separator which utilizes the molecular exchange flow. Knudsen pumps are utilized to supply a pressure difference required for the molecular exchange flow as well as to induce a concentration variation with the molecular exchange flow. The proposed separator is designed to separate gas mixtures by providing only a small temperature difference across membranes. The performance of the separator is analyzed numerically for a two-component gas mixture using the method proposed in [35].

3.2 Operating principles

In this section, I explain the mechanism of the present gas separator. First of all, the flow through a porous membrane is described. In the existing methods of gas separation with porous membranes, the pore size d is much smaller than the mean free path ℓ of gas molecules, so that the Knudsen number $\text{Kn} = \ell/d$ is as large as $\text{Kn} \rightarrow \infty$ [23]. In this case, since the gas molecules tend not to interact with each other, the permeation speeds of component gases only by a pressure difference are proportional to their mean molecular speed, i.e., $(\text{molecular mass})^{-1/2}$. Because a gas with lighter molecules permeates faster than one with heavier molecules, this phenomena is utilized to separate gas mixtures. The pore size of the membrane in the present design is, in contrast, as large as the mean free path, or $\text{Kn} = O(1)$. Therefore, the permeation speeds of component gases are almost the same, which is quite similar to the case of $\text{Kn} \rightarrow 0$ (figure 3.1). Then, the temperature in the high pressure side is increased to induce the thermal transpiration flow in the opposite direction to the pressure driven flow. As the temperature difference increases, the gases begin to permeate from the low pressure side to the high pressure side. A gas with light molecules changes its direction of permeation at a smaller temperature difference than a gas with heavier molecules, because of a nature of the thermal transpiration: the permeation speeds depend largely on the molecular mass as it is driven by the difference of molecular speeds, i.e., a light gas flows faster than a heavy gas. As a result, there exists some temperature difference where one component gas permeates in the opposite direction to another. This is the molecular exchange flow, where a light gas permeates to the high pressure side, and a heavy gas to the low pressure side. This state is denoted as “molecular exchange” in figure 3.1. When I provide a larger temperature difference, all components are pumped from the low pressure side to the high pressure side. It is noted that the membrane has

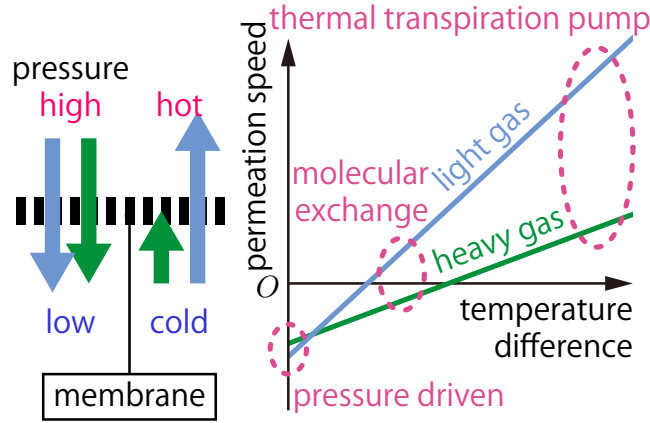


Figure 3.1: The permeation speeds of two component gases through a porous membrane at a fixed pressure difference against the temperature difference. The temperature difference is given so that the high pressure side is heated. The permeation speed is positive when a gas flows from the cold (or low pressure) side to the hot (or high pressure) side. Light/heavy gas represents the gas with lighter/heavier molecules.

separation effect even when it performs as a pump; the permeation speed of a light gas is larger than that of a heavy gas.

The present separator utilizes the molecular exchange flow through porous membranes to induce a concentration variation. However, the temperature difference across membranes cannot be very large, particularly for polymeric membranes like the one used in [17, 45]. Therefore, it is impossible to induce a significant concentration variation only with a small portion of a membrane. Accordingly, the effect of the molecular exchange flow is accumulated using the device shown in figure 3.2, which consists of a pump unit (1), two separator units (2), (3), and a valve. The mechanical structures of the pump unit and the separator units are identical. Each of them is composed of a porous membrane, a heated plate H, and a cooled plate C. A channel is arranged between the membrane and each plate, and allows gas mixtures to flow along the surface of the membrane. It should be noted that the membranes are common to all units, where $Kn = O(1)$ in the pores. The only differences of a pump unit and a separator unit are the size of the membrane and the temperature difference between the H channel and the C channel.

In the pump unit, the temperature difference is set so large that it works as a thermal transpiration pump (figure 3.1): gases are transferred from the C channel to the H channel. Then, the pump unit drives the circulating flow around the membranes of the separator units: the circulation is formed by the pump, the channels H and C of the separator units, and the valve connecting the channels at the right end of the device. The gas supplied by the pump flows in the H channel over the membrane to the valve, and then flows back in the C channel below the membrane. Here, a counter flow setup, which is often used in membrane gas separation devices [23], is implemented in

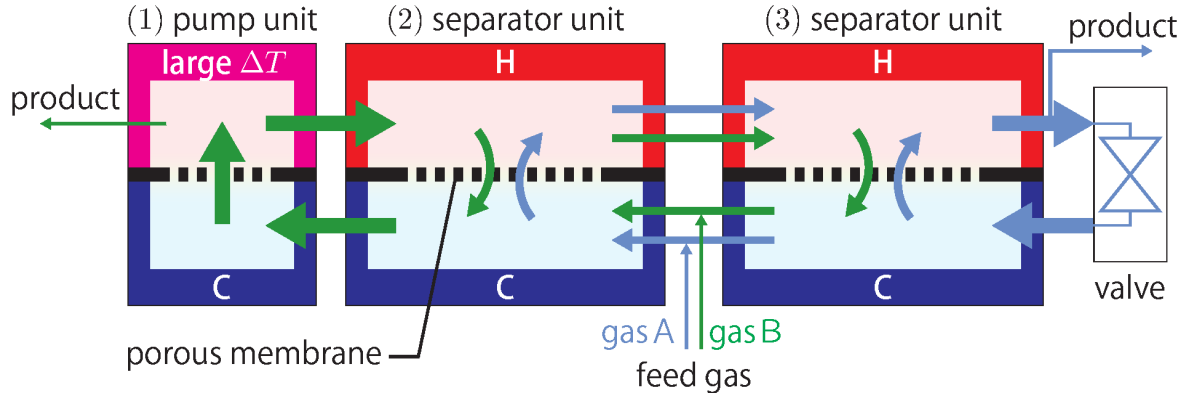


Figure 3.2: Schematic of the present gas separator. The system consists of a pump unit, two separator units and a valve. The pump and the separator have an identical structure, but the pump works at a larger temperature difference than the separator units. The molecules of gas A are lighter than those of gas B.

the device: the gas mixtures, bounded by a thin membrane, flow in opposite directions.

In the separator units, the molecular exchange flow is induced through the membranes. The pressure difference required to induce the molecular exchange flow is provided by the valve at the right end. This flow will affect the composition of gas mixture in the separator units. Since the pressure and temperature in the H channel are both higher than those in the C channel, the molecular exchange flow transfers the light molecules in the direction of $C \rightarrow H$, and heavy molecules in the direction of $H \rightarrow C$. As a result, the mole fraction of light molecules increases downstream (to the right in figure 3.2) in the H channel, and that of heavy molecules increases downstream (to the left) in the C channel. Owing to the counter flow setup, this results in a large concentration variation along the membrane. In this case, the light molecules are concentrated at the right end of the device, and the heavy molecules at the left end. It is also important that the difference of the mole fractions between the channels H and C is kept small over the entire surface of the membrane, because the molecular exchange flow can be easily interrupted by small concentration diffusion. The appropriate speed of the flows in the channels H and C are investigated in the previous chapter.

Finally, gases are produced from both ends, and the equivalent amount of a gas mixture is fed into the separator. The gases are produced from the H channel where the pressure is relatively high, and introduced into the C channel where the pressure is low. This configuration allows the present separator to work continuously by providing only a temperature difference.

3.3 Models and methods of simulation

In the present work, performance of the separator depicted in figure 3.2 is analyzed numerically for a two-component (A and B) gas mixture. The entire separator is repre-

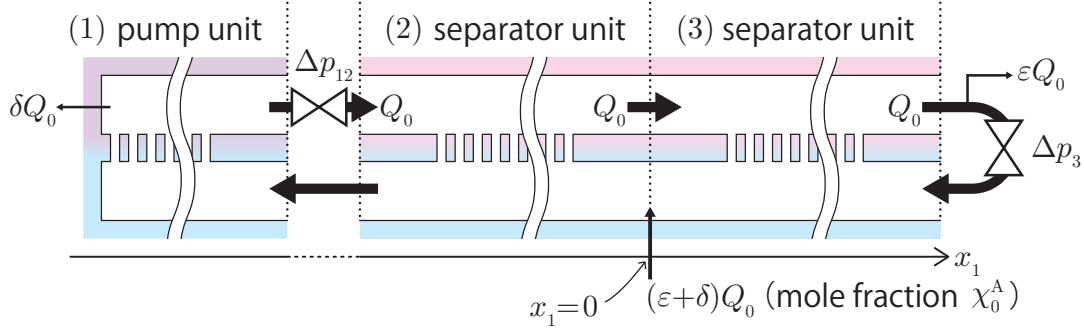
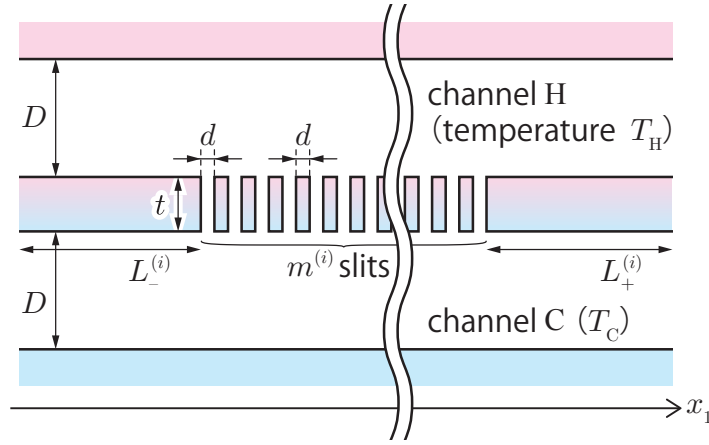


Figure 3.3: Numerical model of the present gas separator.

Figure 3.4: Numerical model of one unit structure of the present gas separator. i represents the number of the unit.

sented by a series of three unit structures (1), (2), and (3) (figure 3.3). The model for one unit structure is composed of two channels and a porous membrane held between them as shown in figure 3.4. The numerical model is two dimensional, and x_1 -axis is taken along the membrane to express the position in the device.

Firstly, the model of each unit structure shown in figure 3.4 is explained. The channels are distinguished by H and C, whose widths are commonly D . The temperature T_C in the C channel is uniform, and the T_H in the H channel may vary gently depending on x_1 . The distribution of T_H is described later. The membrane is modeled as an array of $m^{(i)}$ ($i = 1, 2$ and 3 depending on the number of unit) slits, each of which has width d and length t . The slits are arranged with an interval of d . The wall temperature of each slit varies linearly from T_H to T_C . For simplicity of the numerical procedure, some areas without slits are prepared on the both edges of the membrane. Their lengths are $L_-^{(i)}$ for the space located next to the x_1 -axis negative direction edge of the membrane and $L_+^{(i)}$ for the one next to the positive direction edge.

The entire system shown in figure 3.3 is a series of three units (1), (2) and (3), the

channels of which are connected in a sequence. The flow channel around the membranes in the separator units (2) and (3) is realized by connecting the three units and valves. The C channels of (1) and (2), and the channels H and C in (2) and (3) are directly connected. The H channels of (1) and (2) are connected by a valve to regulate the molecular flux out of the pump for simplicity, where the flux is controlled to be the reference molecular flux Q_0 by a variable pressure drop Δp_{12} . Finally, the H channel and the C channel of the separator unit (3) is connected at the right end by a valve, and the pressure drops by Δp_3 .

Now the molecular exchange condition are considered in each of the separator units (2) and (3): the molecular flux of gas A through the membrane in the direction of C→H equals to that of gas B in the direction of H→C. This condition is realized by equalizing the molecular flux between the influx at the left end and the efflux at the right end in the H channel. The influx into the H channel of (2) is controlled to be Q_0 by manipulating Δp_{12} . The molecular fluxes from (2) to (3) can also be controlled by setting the temperature difference in (2) and (3) slightly differently. The efflux from the H channel of (3) is controlled to be Q_0 by manipulating Δp_3 .

Gases are produced from the left and right ends of the separator at the rates of δQ_0 and εQ_0 . Concurrently, $(\delta + \varepsilon) Q_0$ of feed gas mixture, whose mole fraction of gas A is χ_0^A , is introduced into the C channel at the middle of the separator to conserve the total mass of the mixture in the device.

The separator is initially filled with a gas mixture with density n_0 ($= p_0/\kappa T_C$, p_0 : reference pressure, κ : Boltzmann constant) and mole fraction χ_{initial}^A . Then, the distribution of the partial pressures $p^\alpha(x_1)$, $\alpha = A, B$ is obtained for a steady state using the method proposed in [35] as in the previous chapter.

3.4 Results and discussions

The proposed design is analyzed numerically for neon-argon mixtures, and a set of parameters is found with which the separator works as expected. The width of the slits d is defined so that the Knudsen number ℓ_0^{Ne}/d equals to unity, where ℓ_0^{Ne} is the mean free path of molecules in pure neon gas for the stationary equilibrium state of pressure p_0 and temperature T_C . In this case, d is of the order of 100 nm at standard temperature and pressure. The thickness of the membrane $t = 100d$. The width $D = 2000d$ in the channels H and C. The numbers of the slits in (1), (2) and (3) are $m^{(1)} = 1 \times 10^5$ and $m^{(2)} = m^{(3)} = 2.5 \times 10^5$. The length of the area with no slit $L_-^{(1)} = 2d$ in the left side of unit (1), and $5 \times 10^4 d$ for the others. The ranges of the position x_1 occupied by unit (1), (2), and (3) are respectively $-85 < x_1/10^4 d < -60$, $-60 < x_1/10^4 d < 0$ and $0 < x_1/10^4 d < 60$. The reference molecular flux Q_0 from unit (1) to (2) is set to $d(p_0/\kappa T_C)(2\kappa T_C/m^{\text{Ne}})^{1/2}$, where m^{Ne} is the molecular mass of neon. The value of the flux Q_0 is determined so that the cross-sectional average flow velocity is $0.5 \times 10^{-3} (2\kappa T_C/m^{\text{Ne}})^{1/2}$, which is suitable for inducing large variation of the mole fraction in the separator units [45].

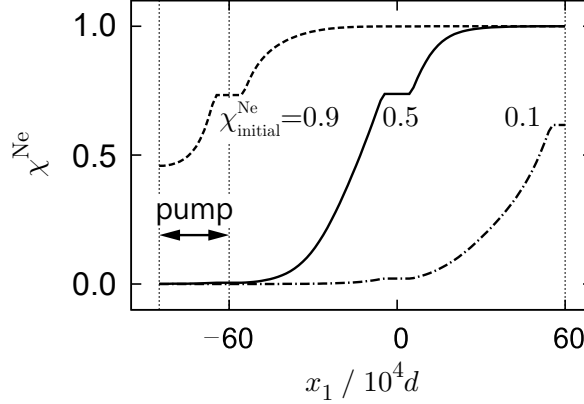


Figure 3.5: The distribution of the mole fraction of neon χ^{Ne} against the position along the membrane $x_1/10^4d$. The position is scaled by 10^4d so that the unit of the abscissas is approximately millimeters at atmospheric pressure.

Since $d (= \ell_0^{\text{Ne}})$ is of the order of 10^{-4} mm at standard temperature and pressure, the total length of the device is around 15 cm. The value of Q_0 corresponds to 27 sccm assuming the width of the separator to be 1 cm, and the corresponding cross sectional average flow velocity is around 0.2 m/s. It is noted that the width has no limitation and the amount of the production can be easily increased.

3.4.1 Cases without production of gases

To begin with, numerical calculations are carried out for the cases without production of gases, i.e., the cases where production rate ε and δ are both zero.

Figure 3.5 shows the distributions of the mole fraction of neon $\chi^{\text{Ne}} \equiv p^{\text{Ne}} / (p^{\text{Ne}} + p^{\text{Ar}})$ along the membrane for $\chi_{\text{initial}}^{\text{Ne}} = 0.1, 0.5$, or 0.9 , which is represented respectively by the dashed line, solid line, and broken line. In these cases, the temperature T_{H} is $1.3T_{\text{C}}$ in the pump part, and around $1.2T_{\text{C}}$ in the separator part, whose distribution is explained in the next section. Regardless of the value of $\chi_{\text{initial}}^{\text{Ne}}$, the distribution of the mole fraction at the steady state is quite non-uniform; neon molecules are concentrated at large x_1 part, and argon molecules at small x_1 part. The variation of χ^{Ne} becomes so large for the case of $\chi_{\text{initial}}^{\text{Ne}} = 0.5$ that χ^{Ne} varies from 0.00 to 1.00, taking a value of 0.74 at $x_1 = 0$. Therefore, pure argon gas or pure neon gas is expected to be produced from each end of the device, if the effect of the production is negligibly small.

3.4.2 Cases with production of gases

When planning to continuously produce gases, appropriate production rates δ and ε has to be determined as the mass of each component in the system conserves at steady states. Writing the mole fraction of neon gas as $\chi_{\delta}^{\text{Ne}}$ and $\chi_{\varepsilon}^{\text{Ne}}$ respectively for the gases

produced at the rates δ and ε , the mass conservation is expressed as

$$\chi_0^{\text{Ne}}(\varepsilon + \delta) Q_0 = \chi_\delta^{\text{Ne}} \delta Q_0 + \chi_\varepsilon^{\text{Ne}} \varepsilon Q_0,$$

or

$$0 = (\chi_\delta^{\text{Ne}} - \chi_0^{\text{Ne}}) \delta + (\chi_\varepsilon^{\text{Ne}} - \chi_0^{\text{Ne}}) \varepsilon. \quad (3.1)$$

This limits the variation in the mole fraction depending on specified δ and ε .

Following the result of the case in the previous section where $\chi_{\text{initial}}^{\text{Ne}} = 0.5$, it seems possible to produce an almost pure gases of neon and argon. As the value of χ^{Ne} at $x_1 = 0$ is 0.74 in that case, I set the mole fraction of the feed gas χ_0^{Ne} to be 0.7. Assuming $\chi_\delta^{\text{Ne}} = 0$ and $\chi_\varepsilon^{\text{Ne}} = 1$, the mass conservation (3.1) requires $\delta : \varepsilon = 3 : 7$. Figure 3.6 shows the results for the case of $\chi_0^{\text{Ne}} = 0.7$ and δ and ε are respectively 0.3 % and 0.7 %, which are expected small enough not to affect the state in the system much.

First of all, the temperature difference $T_{\text{H}} - T_{\text{C}}$ distribution is plotted against x_1 in figure 3.6 (a). The temperature difference is uniformly $0.3T_{\text{C}}$ in the pump unit (1), and varies linearly from $0.26T_{\text{C}}$ at $x_1/10^4d = -60$ to $0.14T_{\text{C}}$ at $x_1/10^4d = 60$ in the separator units (2) and (3). The temperature difference in the device is no more than 90 K at standard temperature and pressure. The variation of the temperature difference in (2) and (3) is explained later in this section.

The distribution of the mole fraction of neon χ^{Ne} in the H channel is shown in figure 3.6 (b). The χ^{Ne} in the C channel is not distinguishable from that in the H channel in the figure to be omitted. The feed gas is introduced at $x_1 = 0$, where the value of χ^{Ne} in C channel is 0.62. It is clearly seen that χ^{Ne} largely varies in the separation units (2) and (3). In addition, χ^{Ne} slightly varies in the pump unit (1). This is because the thermal transpiration pump tends to transfer more light molecules than heavy ones. The purified gases are produced from the both ends of the H channel ($x_1/10^4d = -85$ and 60) at the rate of $0.3\% Q_0$ and $0.7\% Q_0$. The values of χ^{Ne} in the H channel at $x_1/10^4d = -85$ and 60 are respectively $\chi_\delta^{\text{Ne}} = 0.00079$ and $\chi_\varepsilon^{\text{Ne}} = 0.999$. This means that 99.9 mol% argon gas and 99.9 mol% neon gas are produced from the left and right end. The quantities of production are 0.08 sccm for argon and 0.19 sccm for neon, when the width of the separator is 1 cm.

The distribution of the total pressure p is plotted in figure 3.6 (c). In the pump unit (1), the pressure is $\sim 1.08p_0$ in the C channel, and $\sim 1.13p_0$ in the H channel. At the connecting point of (1) and (2) in the H channel, the pressure drops by $\Delta p_{12} \sim 0.043p_0$. Since the pressure decreases as x_1 increases in the H channels of (2) and (3), the gas flows in the x_1 -axis positive direction to the valve. The pressure drops again at the valve by $\Delta p_3 \sim 0.039p_0$, and then the gas flows in the x_1 -axis negative direction in the C channel. Thus, the gas circulates in the device.

Figure 3.6 (d) shows the flux of each gas component through a slit from the C channel to the H channel. Except for the region where the gas is almost pure neon ($x_1/10^4d \gtrsim 40$) or argon ($x_1/10^4d \lesssim -40$), neon gas flows in the direction of C $\rightarrow$ H, and argon gas in the direction of H $\rightarrow$ C. That is, the molecular exchange flow is realized. Since the molecular exchange flow is induced by balancing the pressure difference and

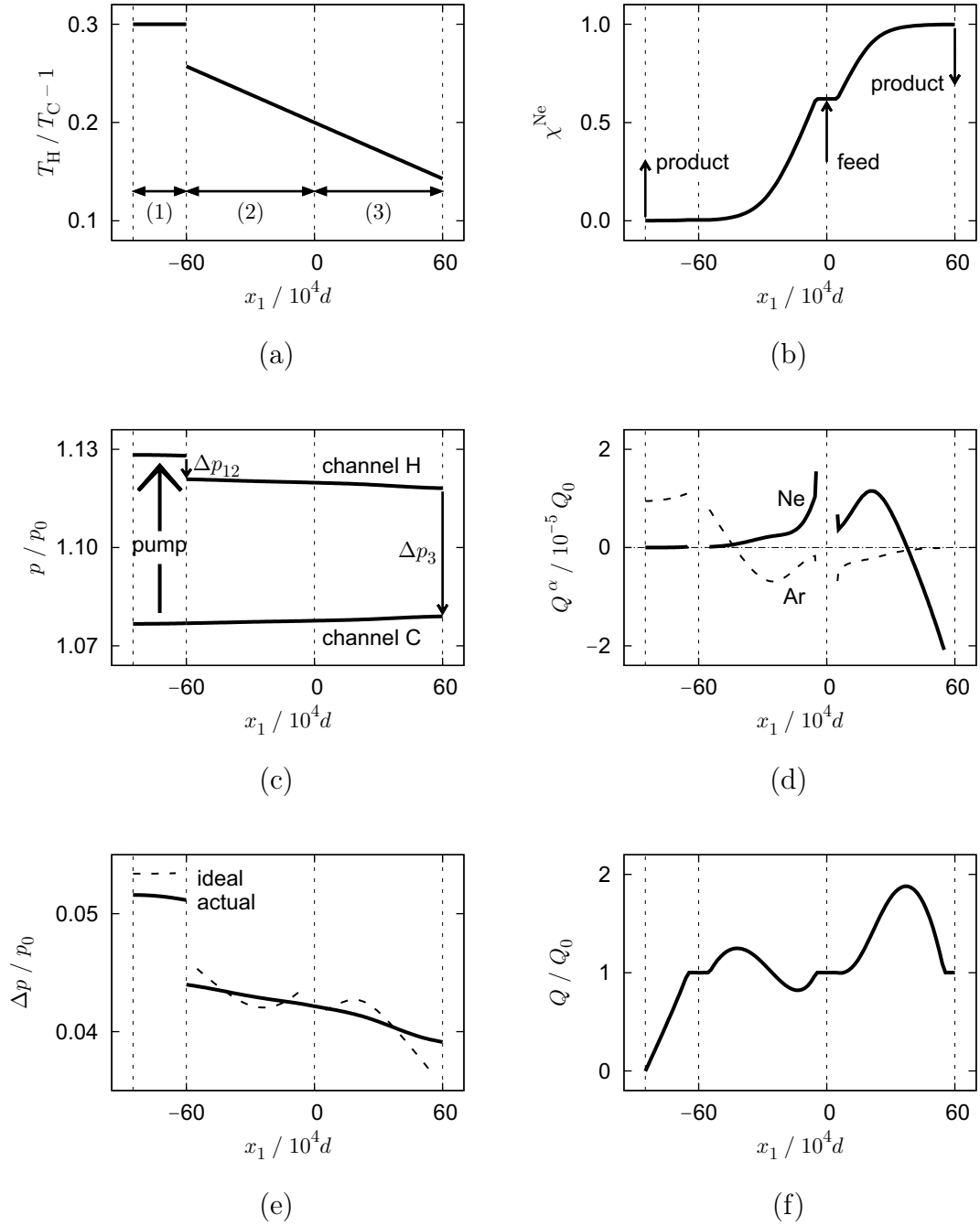


Figure 3.6: Results of a numerical simulation on separation of a 70:30 mixture of neon and argon. The distributions of (a) temperature ratio, (b) mole fraction of neon in H channel, (c) total pressure, (d) flux of each gas component through a slit from the C channel to the H channel, (e) pressure difference between the H channel and the C channel, and (f) molecular flux in the H channel to the x_1 -axis positive direction are plotted against x_1 . The distributions of the concentration and the molecular flux in the C channel are not distinguishable from those in the H channel, and are omitted.

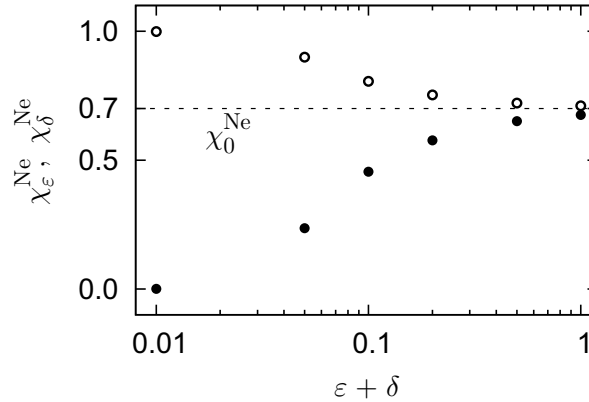


Figure 3.7: The mole fractions of the product gases χ_δ^{Ne} and $\chi_\varepsilon^{\text{Ne}}$ plotted against $\varepsilon + \delta$ for the cases of $\chi_0^{\text{Ne}} = 0.7$ and $\delta : \varepsilon = 3 : 7$. They are represented respectively by solid circles and hollow circles, and the dotted line shows the mole fraction of the feed gas χ_0^{Ne} .

the temperature difference, the difference of the pressures is important in addition to the total pressures in figure 3.6 (c). The actual pressure difference between the channels H and C is shown as the solid line in figure 3.6 (e). It decreases to the x_1 -axis positive direction, i.e., the pressure difference in (2) are larger than that in (3). In order to balance the pressure difference and the temperature difference, the temperature difference in (2) is larger than that in (3) [see figure 3.6 (a)]. However, the sizes of the molecular fluxes of neon and argon are not exactly the same. To clarify the situation, the ideal pressure difference necessary to induce the exact molecular exchange flow, where the total flux of the gas mixture vanishes, is calculated with the temperature difference and the concentration difference of the result. The ideal pressure difference is plotted as a dotted line in figure 3.6 (e). The exact molecular exchange flow is realized through slits at the points of intersection between the ideal and the actual pressure difference: $x_1/10^4 d = -41.9, -13.6, 6.5$, and 37.1 . If the actual pressure difference is greater than the ideal, the pressure driven flow is relatively stronger than the thermal transpiration, and then the gas mixture flows in the direction of $H \rightarrow C$. This results in the decrease of the flux in H channel downstream. In the separator units (2) and (3), the flux fluctuate from Q_0 and the size of fluctuation is up to $88\% Q_0$ as shown in figure 3.6 (f). This is thought to be the result of the linear temperature distribution in H channel, which does not reflect the variation of the viscosity caused mainly by the concentration variation. The temperature distribution must reflect the variation to realize the exact molecular exchange flow, because the viscosity has a strong influence on the pressure distribution along the x_1 axis.

Finally, the effect of the total production rate $\varepsilon + \delta$ is investigated for the cases of $\chi_0^{\text{Ne}} = 0.7$ and $\delta : \varepsilon = 3 : 7$. Figure 3.7 shows the dependence of χ_δ^{Ne} (solid circles) and $\chi_\varepsilon^{\text{Ne}}$ (hollow circles) on $\varepsilon + \delta$, along with χ_0^{Ne} represented by the horizontal dotted line.

The case for $\varepsilon + \delta = 0.01$ is the one explained above, where almost pure neon and argon gases are produced. The difference between the mole fractions of the feed gas and each product gas remains as large as several tens of percent for the total production rate of one tenth. As the total production rate approaches to unity, the mole fractions of the product gases become closer to that of the feed gas.

3.5 Conclusion

A design of membrane gas separator which operates by providing only a small temperature difference across membranes is proposed. The separator system consists of three Knudsen pumps connected in series, each of which is composed of a porous membrane and one channel along each of the two surfaces of the membrane. By controlling the temperature difference between the two surfaces of the membrane, each unit can operate either as a separator unit or as a pump unit. In a separator unit, the temperature difference is controlled to balance with the pressure difference, so that the molecular exchange flow is induced through the membrane. In a pump unit, the temperature difference is larger than that in the separator units, and the gas is transferred from the low temperature side of the membrane to the high temperature side by the thermal transpiration. The pump unit drives the circulating flow around the membranes of the separator units. This circulating flow accumulates the concentration variation caused by the molecular exchange flow in the separator units. As a result, a large concentration variation is induced between the left and the right end of the device. The present design is free from the fundamental restriction of the existing methods of membrane gas separation: all component gases permeate in the same direction through membranes.

Two-dimensional numerical calculations are carried out for the case where a gas mixture of 70 mol% neon and 30 mol% argon is fed into the separator. The separator is ~ 15 cm long, and the temperature difference is no more than 90 K at standard ambient temperature and pressure. It is demonstrated that the gas mixture can be separated into 99.9 mol% argon gas and 99.9 mol% neon gas without any by-product, when the total amount of the production is 1 % Q_0 , where Q_0 is the molecular flux flowing out of the pump unit. The mole fraction of the product gases remains significantly different (more than 10 mol%) from that of the feed gas when the total amount of the production is increased to 10 % Q_0 . The amounts of production are proportional to the width of the membrane. For example, when the width of the separator is 1 cm, the amounts for 1 % Q_0 are 0.08 sccm for argon and 0.19 sccm for neon. It is also noted that a binary feed gas mixture of $(\delta + \varepsilon) Q_0$ is simply separated into the pure gases of δQ_0 and εQ_0 , and no other by-product exists.

Chapter 4

Demonstration of Gas Separator

4.1 Introduction

Challenges to reduce the energy costs of separating gas mixtures lead to the developments of various novel separation methods. The membrane gas separation has advantages of mechanical simplicity, separation without phase transition, operation near the ambient conditions, and continuous nature of its process [23,46,47]. Most of the research on membrane gas separation deals with one of three molecular transport mechanisms, Knudsen diffusion, solution diffusion, and molecular sieving, induced by the pressure difference across the membrane. Mixtures of gas species are separated based on the difference in the speed of the molecular transport: the smaller molecules generally diffuse faster than larger molecules except for the membranes with reverse selectivity [48], in which larger molecules diffuse faster. Relying only on these pressure-driven molecular transport mechanisms, the selectivity, which is the ratio of the permeabilities of fast and slow molecules, has decisive importance in the membrane gas separation. The production of high purity gas is difficult because the direction of molecular transport is determined by the pressure difference. At present, chemical science plays an essential role in improving the selectivity and permeability of non-porous or nanoporous membranes for solution diffusion or molecular sieving [24,49,50].

Contrary, in view of the vacuum technology, e.g., molecular gas dynamics or rarefied gas dynamics, pressure difference is not the only driving force of the molecular transport in micro- or meso- porous membranes. When the mean free path of gas molecules is not negligible compared to the pore size of the membrane, the temperature difference also induces various gas flows characteristic to the rarefied gas [1,15,27,51–53]. A well-known example is the thermal transpiration flow [1,2,7,10,11,15,27] through a pipe with the temperature gradient along its axis.

It is very important that multiple driving forces of molecular transport are available, which are the pressure difference and the temperature difference here. Take, for example, a binary gas mixture. The speed ratio of pressure driven flow between two species is generally different from that for temperature driven flow since the physical mechanisms of molecular transport are quite different. In this case, superposing the two

flows with appropriate pressure and temperature differences, the speeds of the molecular transport of two species can take arbitrary ratio. Theoretical analysis shows the possibility of the molecular exchange flow [19, 54], where the molecules of two different species are exchanged through the channel. The gas separation by the molecular exchange flow is a promising method since it is free from the restriction of the selectivity of the membrane [26] and has possibility of producing high purity gases.

Experimental studies to induce the temperature driven flows of rarefied gas have been carried out in relation to the development of Knudsen pump [17, 29, 55–62], a motionless pump driven by the thermal transpiration flow. The key to the Knudsen pump for gases at standard pressure is to maintain the appreciable temperature variation in the scale of the mean free path of gas molecule, which is as small as 10^{-7} m at standard condition. In 2011, Gupta and Gianchandani [17, 60] devised a Knudsen pump using MCE membranes, which is commonly used as filter papers. Their dime-sized pump showed an outstanding performance; the flow rate is around 1 sccm and the pressure difference is 1 kPa by a temperature difference of 30 K at atmospheric pressure. This achievement enabled the experimental demonstration of the molecular exchange flow in [45], where a piece of MCE membrane of 30×30 mm size is used. The molecular exchange flow is driven by the temperature difference of 45 K and the pressure difference of 5 kPa, and the effect is accumulated by counter flow of feed gas around the membrane to induce 15 % variation of mole percentage of a helium–argon mixture.

Another advantage of the Knudsen pump using membrane is the feasibility of the system driven by low-grade waste heats. As described above, the pump operates with several tens of degrees of temperature difference. Electricity is used in [17, 45, 60] only to heat one side of the membrane, and can easily replaced by another heat source. Since plenty of heat energy is available in a form of temperature difference about 100 K as low-grade waste heat of industrial processes, the cost of energy for the membrane separation can be reduced.

The present experiment aims to demonstrate the basic concept of the gas separation method proposed in our previous numerical study [63]. The gas separator there consists of several Knudsen pumps. The system works only with small temperature differences and does not require pressure differences, which is provided externally in the previous experiment [45]. The goal is to produce two gases of different mole percentages continuously from a feed mixture. This is the very first experimental study on the membrane gas separator enhanced with the thermal transpiration; therefore, the feasibility of the basic concept is investigated only for a binary mixture of noble gases: helium–neon mixture. Two Knudsen pumps similar to that developed in [45] are used in the present work.

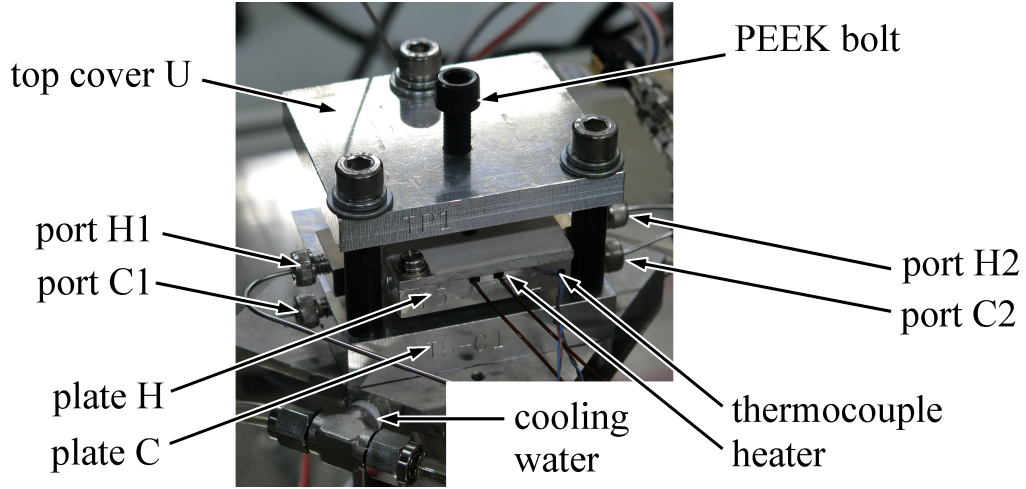


Figure 4.1: Overview of the Knudsen pump used in the present gas separator. (KP1 in figure 4.7).

4.2 Gas separation system

4.2.1 Knudsen pump device

The present gas separator consists of several units of Knudsen pump. Their design is based on the pump devised in [45]. Figure 4.1 is the photograph of a pump device, and its exploded view is shown in figure 4.2. Two aluminum plates H and C sandwich several sheets including the thermal transpiration membrane at the middle. The thermal transpiration membrane is a MCE membrane (Advantec MFS Inc. A010A047A), whose size is 33×33 mm. The plate H is heated by an electric heater. The plate C is put on an aluminum plate cooled by water or airflow. Heat-dissipating silicone grease is applied when mounting the heater and cooler. The temperatures of plates H and C are monitored by thermocouples.

The temperature of the surface of the membrane is kept close to that of plate H or C by the heat conducted through a wire mesh unit, which is explained later. The circumference of the sheet and mesh unit is sealed by two square fluoro-rubber rings. The inner size of the rubber ring is 30×30 mm, and each plate H or C has a stage that fits in the ring. The wire mesh units are slightly smaller than the inner size of the rubber ring. Therefore, the MCE membrane is held between the wire mesh units on the stages of H and C in the rubber ring. The sides of the membrane are sealed by the rubber rings, whose inner size is slightly smaller than the size of the membrane. The structure shown in figure 4.2 is pressed from above by a top cover U and a PEEK bolt as shown in figure 4.1.

The inlet and outlet for the gas flow are prepared as two trenches (opening size 25×1 mm, depth 4 mm) on each of plates H and C (see figure 4.2). The distance between two trenches is 25 mm. Each trench is connected to a stainless tube, and

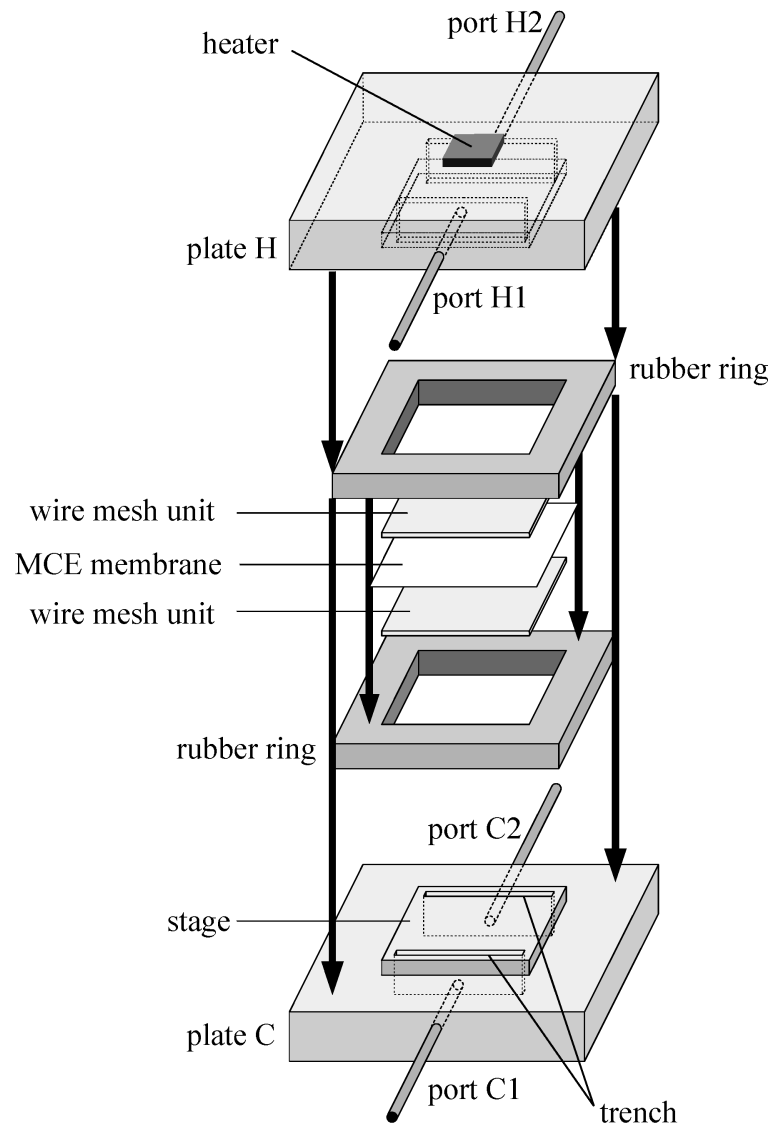


Figure 4.2: The exploded view of the Knudsen pump.

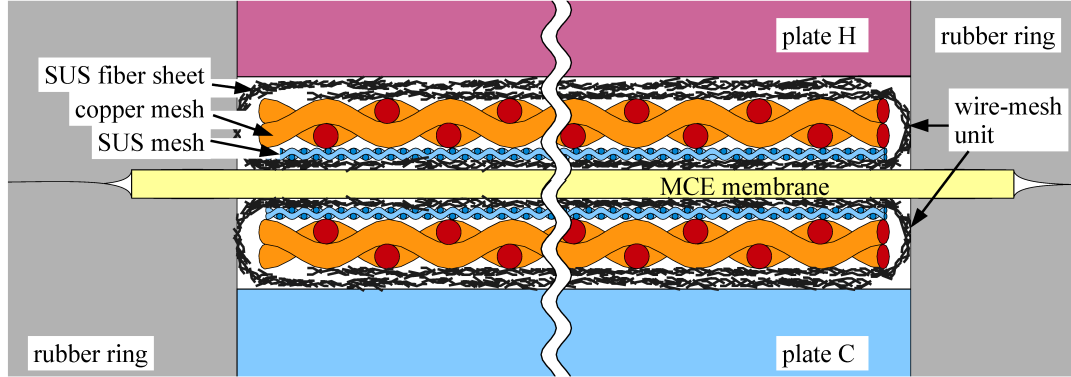


Figure 4.3: Schematic of the device structure around MCE membrane.

the four stainless tubes work as gas ports. The H1 and H2 ports are located on H side, and C1 and C2 ports are on C side. The wire mesh unit is prepared so that the gas supplied from these ports can flow along the membrane. The inner structure of the device around the MCE membrane is shown schematically in figure 4.3. Each wire mesh unit consists of a sintered SUS fiber sheet (Tomoegawa Paper Co. Ltd., Tomifleck SS2-150H), a SUS mesh, and a copper mesh. And the fiber sheet wraps other meshes. Their specifications are shown in table 4.1. figure 4.4 is the photograph of the mesh unit. The copper mesh is employed to make the space for the gas flow. From now on, the space adjacent to plate H (C) is denoted by channel H (C). Other meshes are prepared to press the membrane uniformly, conduct the heat from plates H and C to the membrane, and provide sufficient gas flow to the membrane.

Table 4.1: The product specifications of the sheet materials used in the Knudsen pump.

part name	material	thread or pore size	thickness	porosity
MCE membrane	MCE	0.1 μm (pore size)	110 μm	65 %
SUS fiber sheet	SUS316	8 μm	34 μm	80 %
SUS mesh	SUS316	25 μm	50 μm	70 %
copper mesh	copper	100 μm	200 μm	60 %

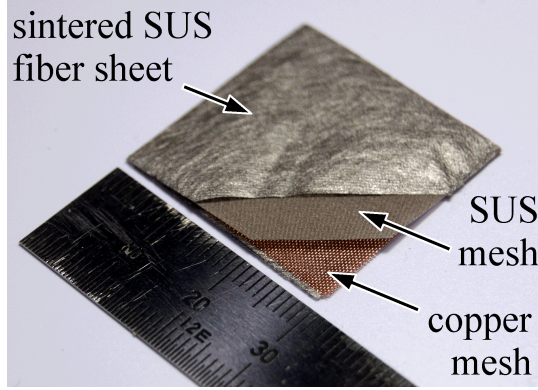


Figure 4.4: Photograph of the wire mesh unit. Some part of outer meshes are removed to show the inner structure of the unit. Upper side faces to MCE membrane in the device.

4.2.2 Mixture flow through the Knudsen pump

The gas flow in the Knudsen pump depends on the pressure and temperature differences between two channels H and C. The flow through the membrane is in a rarefied regime since the pore size ($0.1 \mu\text{m}$) is close to the mean free path of gas molecules at atmospheric pressure. As a result of small pore size, the flow speed through the micro-channel is slow and the state of the gas remains close to a reference uniform state, which enables the treatment with the linear theory of the molecular gas dynamics or the Boltzmann equation [7]. In the case of a binary mixture of gases A (molecular mass m^A) and B (m^B), the average speed of molecules U^α of α -gas ($\alpha = A, B$) through the micro-channel of diameter d is given by

$$U^A = c_0^A d \left[U_T^A \frac{T'}{T_0} + U_p^A \frac{p'}{p_0} + U_\chi^A \frac{\chi'}{\chi_0} \right], \quad (4.1a)$$

$$U^B = c_0^B d \left[U_T^B \frac{T'}{T_0} + U_p^B \frac{p'}{p_0} + U_\chi^B \frac{\chi'}{100 - \chi_0} \right], \quad (4.1b)$$

where T and p are the temperature and pressure of gas mixture, respectively, χ is the mole percentage of A gas, and c^α is the most probable speed of α molecules [$c^\alpha = \sqrt{2\kappa T/m^\alpha}$ (κ : Boltzmann constant)]. The values with subscript zero indicate the values at the reference state of the gas (pressure p_0 and temperature T_0 at rest), and those with prime indicate the gradients along the micro-channel. Here, I assume $m^A < m^B$ to avoid confusion. The non-dimensional coefficients U_T^α , U_p^α , and U_χ^α are obtained by the linear analysis of the Boltzmann equation [7, 10–13]. These values depend on the molecular model (including the mass ratio m^B/m^A), reference mole percentage χ_0 , and the Knudsen number Kn at the reference state:

$$\text{Kn} = \ell_0/d, \quad (4.2)$$

where ℓ_0 is the equivalent free path of gas molecules defined by

Table 4.2: Example of the theoretical values of $U_{\#}^{\alpha}$. The case for helium-argon mixture ($\sqrt{m^B/m^A} \approx 3.16$) in [10] (hard-sphere molecules) and the case for neon-argon mixture ($\sqrt{m^B/m^A} \approx 1.41$) in [11, 12] (McCormack realistic model of molecules). The shape of the cross section is shown by $\bigcirc$: circular pipe of diameter d , $\square$: square of side d , $\parallel$: 2D channel of width d .

A-B, shape	χ_0	$\text{Kn} = \frac{\ell_0}{d}$	$-U_p^A$	$\frac{U_p^A}{U_p^B}$	U_T^A	$\frac{U_T^A}{U_T^B}$	$-U_{\chi}^A$	$-\frac{U_{\chi}^A}{U_{\chi}^B}$
He-Ar, $\bigcirc$	50	0.0125	1.20	1.01	0.00553	2.61	0.00966	3.55
		0.25	0.266	1.54	0.0668	3.08	0.132	3.37
		1.25	0.303	2.45	0.122	3.25	0.259	3.24
		500	0.376	3.16	0.188	3.16	0.376	3.16
Ne-Ar, $\square$	50	1	0.364	1.25	0.128	1.42	0.252	1.41
Ne-Ar, $\parallel$	10		0.680	1.21	0.186	1.43	0.401	1.43
	50		0.712	1.19	0.183	1.43	0.378	1.43
	90		0.760	1.16	0.182	1.41	0.349	1.43

$$\ell_0 = \frac{\mu_0 \sqrt{2kT_0/m}}{p_0}, \quad (4.3)$$

where μ_0 is the viscosity of the mixture [64] and m is the mean mass of a molecule: $m = \chi_0 m^A + (1 - \chi_0) m^B$.

Several examples of the values of $U_{\#}^{\alpha}$ ($\# = p, T$, and χ) taken from the references are presented in table 4.2 along with the values of speed ratio between the species $U_{\#}^A/U_{\#}^B$. The dependency of $U_{\#}^{\alpha}$ on Kn can be seen from the data for helium-argon mixture in circular tube [10]. The behavior of the speed ratio $U_{\#}^A/U_{\#}^B$ for the thermal transpiration and the diffusion is different from that for the pressure driven flow. The values of U_T^A/U_T^B and U_{χ}^A/U_{χ}^B are close to the speed ratio of the thermal speeds of molecules $\sqrt{m^B/m^A} \approx 3.16$ for any Knudsen number. In contrast, the value of U_p^A/U_p^B depends on the Knudsen number. Its value is around $\sqrt{m^B/m^A}$ only for large Kn, and it converges to unity as $\text{Kn} \rightarrow 0$. This is because the pressure driven flow does not vanish but diverges as $\text{Kn} \rightarrow 0$, where the frequent intermolecular collisions make the flow speeds of component gases indistinguishable. The other flows, the thermal transpiration flow U_T^{α} and diffusion U_{χ}^{α} vanishes there. For the intermediate Knudsen numbers, the size of the pressure driven flow U_p^{α} and the thermal transpiration flow U_T^{α} remain in the same order, and concomitantly they have different speed ratios $U_{\#}^A/U_{\#}^B$. This is a general feature of gas flow in micro-channels as it can be seen from the data given in table 4.2 for different gas mixture, cross section, and mole percentages [11, 12].

The difference of speed ratios enables us to determine the flows of each component gas. For example, the non-dimensional flow speeds of gas components $U^{\alpha}/c_0^{\text{He}}$ [Eqs. (4.1a) and (4.1b)] is plotted in figure 4.5 for the case of helium-argon mixture ($\chi_0 = 50\%$). In this figure, the case for $dp'/p_0 = 10^{-5}$ and $\chi' = 0$ is considered, and thus the

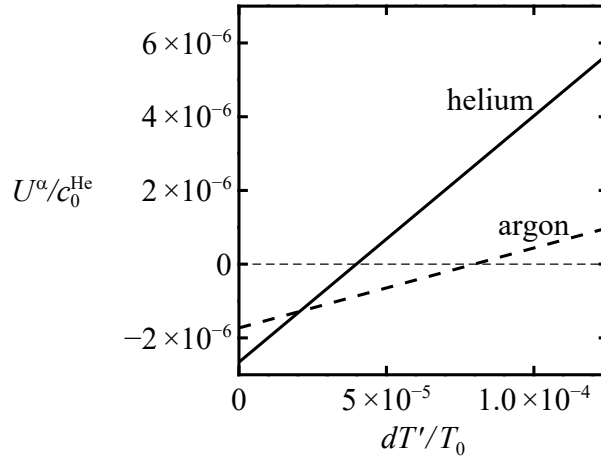


Figure 4.5: The flow speeds of component gases U^α through the micro-channel versus the nondimensional temperature gradient dT'/T_0 along the tube for helium-argon mixture with mole percentage 50 % [10]. The nondimensional pressure gradient is set to $dp'/p_0 = 10^{-5}$. Both of the gradients T' and p' are positive in this figure to show the possibility of the molecular exchange flow (around $dT'/T_0 \approx 5 \times 10^{-5}$) and the pump flow (for $dT'/T_0 \gtrsim 10^{-4}$).

flow speed is determined by dT'/T_0 . Incidentally, as for the actual device shown in figure 4.2 under the standard condition ($p_0 = 10^5$ Pa and $T_0 = 273$ K), $dp'/p_0 \approx 10^{-5}$ and $dT'/T_0 \approx 10^{-4}$ corresponds to 1 kPa pressure and 30 K temperature differences across the membrane of thickness $t = 100 \mu\text{m}$ and pore size $d = 0.1 \mu\text{m}$. The value of $U^\alpha/c_0^{\text{He}} \approx 10^{-6}$ corresponds to a flow speed around 1 mm/sec and to a flow rate of about 30 sccm for the membrane of 30×30 mm size with 60% porosity. At the isothermal state $T' = 0$, both of helium and argon flows in the opposite direction of the pressure gradient. The flow speed increases as T' increases due to the thermal transpiration, and its effect is larger for smaller molecules, i.e., helium. As a result, at $dT'/T_0 \approx 0.5 \times 10^{-4}$, the flow speeds satisfies

$$U^{\text{He}} + U^{\text{Ar}} \approx 0. \quad (4.4)$$

That is, the same number of helium and argon molecules are exchanged through the micro-channel, and the molar flux of the mixture vanishes. This state is called “molecular exchange flow” through micro-channels [19]. For larger temperature gradient, both of helium and argon flows in the same direction from the cold part to the hot part, which means the membrane works as a pump (Knudsen pump). It is also noted that the mass transport induced by the Knudsen pump depends much on species; the small molecules flow faster.

The key to the molecular exchange flow is the presence of two flows based on different mechanisms: the pressure driven flow and the thermal transpiration flow. The total molar flux through the micro-channel vanishes under appropriate values of the pressure and temperature gradient p' and T' , but the component velocities do not vanish

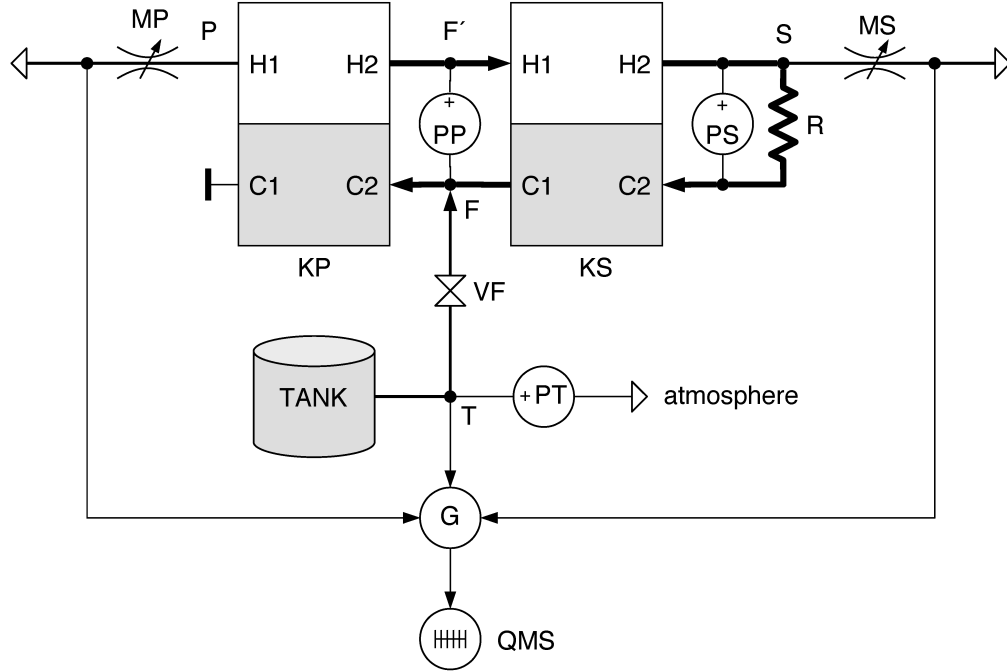


Figure 4.6: The diagram of the gas separator system by two Knudsen pump KP and KS. The differential pressure sensors are indicated by PP, PS, and PT. R is the flow resistance. The gas mixture is supplied from the tank at point F into the system through the valve VF, which is kept open in the experiment. Product gases are taken from ports P and S, and their flow rates are controlled by mass flow controllers MP and MS. The sampler G can sample a gas from S, P, or T. The compositions of the sampled gas is analyzed by QMS.

simultaneously.

4.2.3 Gas separation system

Figure 4.6 is the diagram of the gas separator system, which comprises two Knudsen pumps, KP and KS. The device KP is operated at relatively larger temperature difference ΔT_P between the H and C plates so that it works as a pump. The pump transports the mixture from the low-pressure port C2 to the high-pressure port H2. The gas is then led to the other Knudsen pump KS, which is operated at relatively smaller temperature difference ΔT_S so that it induces molecular exchange flow through its membrane. Under the molecular exchange condition (4.4), the net volume flow through the membrane vanishes. Therefore, the volume flow rates at H1 and H2 ports are the same. The gas discharged from port H2 flows into the resistance R where the pressure drops to supply KS with the pressure difference required to induce the molecular exchange. The low pressure gas out of R is returned into port C2 of KS. Owing to the molecular exchange

in KS, the same volume of mixture gas flows out of the port C1 of KS. Finally, the mixture returns to port C2 of KP. In short, the gas mixture circulates through the system.

The product gases are taken from the two ends of the system indicated by P and S in figure 4.6. The mass flow of the product can be controlled by two precision mass flow controllers (Fujikin Incorporated FCS-T2000. Full scale (for nitrogen) 5 sccm and accuracy is 0.0125 – 0.05 sccm depending on the flow rate) MP and MS. Exactly the same amount of feed gas has to be supplied into the system since the internal volume of the gas separator is quite small (below 5 cm³ including the tubings). This requirement is fulfilled by connecting a tank (inner volume 8000 cm³) to the system at point F via valve VF as in figure 4.6. Initially the VF is closed and the tank is filled with the feed gas mixture of higher pressure (about twice of the atmospheric pressure). The valve VF is kept open during the experiment so that the pressure at F is the same as that in the large tank which is not sensitive to the size of product flows. The variation of the pressure p_T and temperature T_T in the tank is measured by, respectively, a differential pressure sensor PT (Honeywell ASDXRRX030PDAA5) and a thermistor (Semitek JT103) attached to the tank.

In the above setup, there are two types of gas flow in device KS. The first one is the counter flow along the membrane: the mixture flows $H1 \rightarrow H2$ in channel H, and $C2 \rightarrow C1$ in channel C. The other one is the molecular exchange flow, where the helium flows $C \rightarrow H$ while neon flows $H \rightarrow C$ through the micro-channels in the membrane. As shown in the previous experiments in [45], the combination of these flows induces a variation of the gas composition along the membrane. The smaller helium gas is concentrated to the side of H2 and C2 (referred to as 2-end in short from now on) and heavier neon gas is concentrated to the side of H1 and C1 (1-end). The mole fraction varies due to the accumulation based on the convection effect of the counter flow, where the effect plays a significant role only for a limited range of the speed of the counter flow around 0.1 – 1 m/s. For smaller speed of counter flow, the effect of the molecular exchange diffuses in the channels H and C and is not accumulated. For larger speed of counter flow, the effect of the molecular exchange is diluted and variation of mole percentage vanishes.

Since the experiment [45] is carried out by only one device KS, the gas mixture flows out of C1 port of device KS is exhausted into the atmosphere. As the result, almost all of the feed gas is wasted except a small amount of the gas taken from H2. In the present setup, the outflow from KS is reused by the pump device KP, which helps us to get rid of the loss of the feed gas mixture. Another purpose of KP is to concentrate large molecules. This effect is important for the gas separator: if there is no variation of the gas composition at P, the variation at S also vanishes due to the mass conservation. As is seen from figure 4.5, the flow rate of Knudsen pump is larger for smaller molecules. Therefore, helium is pumped up in prior to neon near 2-end of KP, and neon gas is concentrated left near 1-end (i.e., point P of the system).

The pressure difference required to be induced in KP is larger than that in KS. Therefore, different heaters and coolers are used for these devices. The rated heating

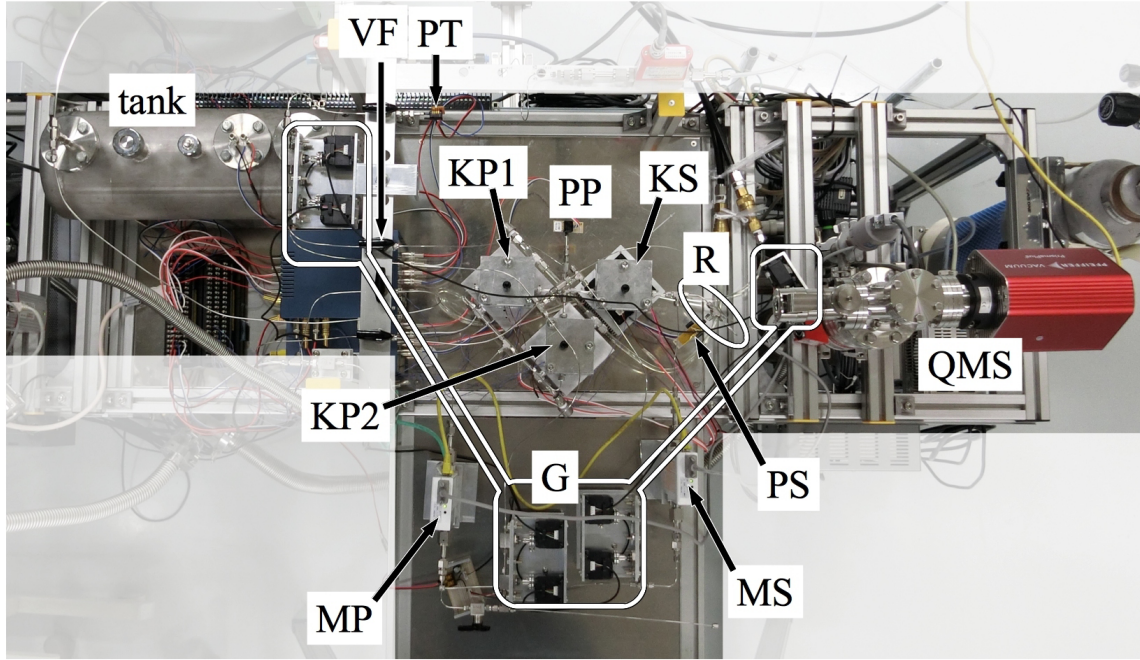


Figure 4.7: Top view of the experimental system.

power of the heater is 100 W for KP (Micro Ceramic Heater MS-1 by Sakaguchi E.H VOC Corp.), and 40 W for KS (MS-3). Water cooling is adopted for KP while air cooling fan is used for KS. Despite these differences, however, large area of MCE membrane is required for device KP to induce sufficient circulating flow through H and C channels. Therefore, parallel connection of two pump units is employed, where KP is a parallel connection of KP1 and KP2 as in figure 4.7. The area of the membrane is 18 cm^2 for device KP and 9 cm^2 for KS. The pressure difference induced by KP is measured using a differential pressure sensor PP (Honeywell ASDXRRX010NDAA5). The pressure drop caused by the flow resistance R (1/16" SUS tube of length 9 cm) is measured using a differential pressure sensor PS (All Sensors, 1INCH-D-4V).

The composition of the gas mixture is analyzed by the QMS (Pfeiffer QMG220) with a metal dosing valve (Pfeiffer UDV040). It is connected to a gas sampling system G, which can sample about 0.026 cm^3 of gas from one of its three ports. Therefore, we can analyze the composition of the gas at three points T, P, and S shown in figure 4.6. Since the point T is between the tank and the valve VF, the composition of the gas in the tank can be analyzed for reference when VF is closed. During the experiment, the valve VF is open and the feed gas flows slowly from the tank to the gas separation system. The mole percentage of helium of the feed mixture sampled from port T is denoted by χ_0 , and those of the product gas from ports P and S are denoted respectively by $\chi_0 + \Delta\chi_P$ (port P) and $\chi_0 + \Delta\chi_S$ (port S).

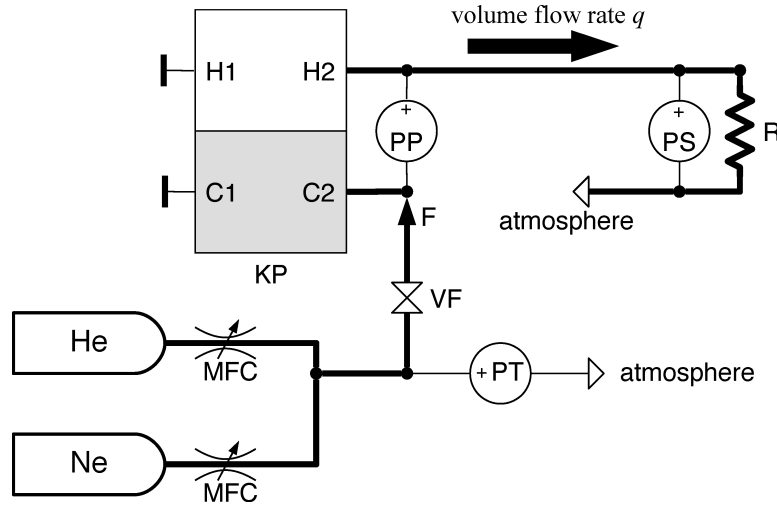


Figure 4.8: The diagram of the calibration experiment.

4.3 Method of experiment

4.3.1 Calibration

The key to the present experiment is the molecular exchange state in device KS, which means the net volume flow through the membrane vanishes. The molecular exchange state is easily ensured to be established by balancing two volume flow rates at H1 and H2 of KS. These flow rates can be measured by pressure sensors PP or PS with the data of the calibration experiments described below.

The apparatus for the calibration experiment is shown in figure 4.8. Compared with figure 4.6, KS is removed, one end of R is directly connected to H2 port of KP, the other end of R is open to the atmosphere, and the gas mixture is supplied from cylinders through two mass flow controllers (indicated by MFC in the figure). In the present apparatus, the mixture from cylinders flows through the pump KP and then the flow resistance R. Because this experiment requires a fairly large amount of the gas, the gases are supplied from cylinders and the precision mass flow controllers MP and MS are not used.

The volume flow rate q passing through KP and R is controlled by MFCs. The performance of KP, i.e., the relation between q and the pressure rise Δp_P from C2 port to H2 port, can be measured by the pressure sensor PP. The result can be approximately written as [45]

$$\Delta p_P = C_1 (p_{\text{env}}, \chi) q + C_2 (p_{\text{env}}, \chi) \Delta T_P, \quad (4.5a)$$

where the p_{env} is the pressure of the atmosphere. At the same time, the pressure drop $\Delta p_S (> 0)$ given by R for the volume flow rate q is measured by PS, and their relation can also be written as

$$\Delta p_S = C_3 (p_{\text{env}}, \chi) q. \quad (4.5b)$$

The coefficients generally depend on the mole percentage χ of helium of the mixture, which can be controlled by MFCs. The data of C_1 , C_2 , and C_3 will be used in the process of main experiment in the next section.

4.3.2 Procedure of experiment

The main experiment starts with closing the valve VF and filling the feed tank with 50 %v/v helium-neon gas mixture. The pressure in the tank p_T at this stage is around 1.5 atm. The next step is to remove the residual gas in the test system by opening the valve VF and exhausting the gases through the mass flow controllers MP and MS. The residual gas is removed through MP and MS, and the system is filled with the feed gas. The completion of this process is confirmed by QMS, and then the flows through MP and MS are controlled to some given flow rates of the product gases. The heaters of devices KP and KS are initially off.

Next, the heater of KP is turned on. The electric current is controlled so that the temperature difference ΔT_P between H and C plates of device KP is around 100 K. The volume flow rate q_P induced by KP can be calculated using (4.5a):

$$\Delta p_P = C_1 (p_{\text{env}}, \chi_0 + \Delta \chi_P) q_P + C_2 (p_{\text{env}}, \chi_0 + \Delta \chi_P) \Delta T_P. \quad (4.6a)$$

The values of C_1 and C_2 depend on the gas pressure in the test device. There are two choices for the pressure value in the system given in figure 4.6: the pressure p_T in the tank and the atmospheric pressure p_{env} . p_{env} is used for the pressure values since p_T is close to the atmospheric pressure. Some part of the gas flowing out of device KP passes through the membrane of device KS, while the other part flows through R. The volume flow rate q_S through R is calculated using (4.5b):

$$\Delta p_S = C_3 (p_{\text{env}}, \chi_0 + \Delta \chi_S) q_S. \quad (4.6b)$$

This process is indicated by $O \rightarrow 1$ in figure 4.9, which shows schematically the traces of $(q_P, \Delta p_P)$ and $(q_S, \Delta p_S)$ in the experiment.

The final step is to supply the heat to device KS. The temperature difference ΔT_S induces the thermal transpiration flow in the direction $C \rightarrow H$ in device KS; this increases the volume flow rate q_S through R and the pressure differences Δp_P and Δp_S . As the result, q_P decreases since $(q_P, \Delta p_P)$ must satisfy (4.6a), while q_S increases with Δp_S as (4.6b). Therefore, an appropriate temperature difference ΔT_S can be found

$$q = q_P = q_S, \quad (4.7)$$

as indicated by symbol 2 in figure 4.9, where we can expect the molecular exchange flow in device KS. It is noted that the values $\Delta \chi_P$ and $\Delta \chi_S$ used in (4.6a) and (4.6b) are updated during the experiment, while the mole percentages are obtained over a long interval in order to avoid the effect of the residual gases in the tubings of the sampling system G.

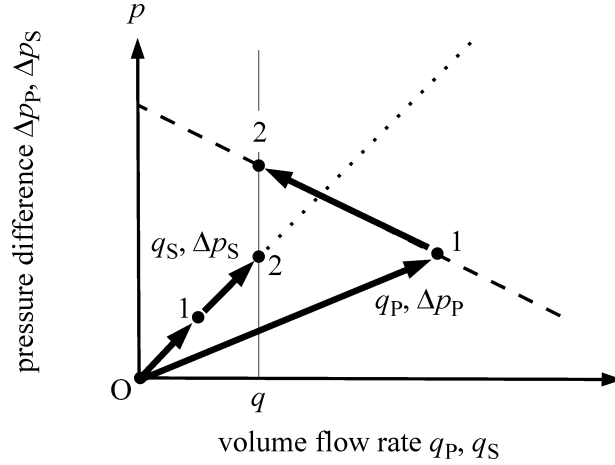


Figure 4.9: Process of the main experiment. Schematic of the traces of $(q_P, \Delta p_P)$ and $(q_S, \Delta p_S)$. The dashed line indicates the relation (4.6a) of pump device KP, and dotted line indicates the flow resistance of R given by (4.6b).

Finally, I discuss the flow rates of the product gas taken out through the two mass flow controllers, MP and MS. The volume flow rates through MP and MS are denoted by Q_P and Q_S , respectively. Then $Q = Q_P + Q_S$ is the total flow rate through the gas separator system, which must be fairly smaller than the internal circulating flow rate q :

$$Q \ll q.$$

The ratio of Q_P and Q_S relates to the mass conservation. It is noted that the mole percentage of the gas at point F, or $\chi_0 + \Delta\chi_F$, can be different from χ_0 of the feed gas, since small size of Q may lead large effect of diffusion in the tubings between point F and tank. The mass conservation of helium molecules at steady state leads

$$Q(\chi_0 + \Delta\chi_F) = Q_P(\chi_0 + \Delta\chi_P) + Q_S(\chi_0 + \Delta\chi_S),$$

that is,

$$\Delta\chi_F = \left(1 - \frac{Q_S}{Q}\right) \Delta\chi_P + \frac{Q_S}{Q} \Delta\chi_S. \quad (4.8)$$

Therefore, we can estimate the mole percentage $\Delta\chi_F$ from the values of Q_S , Q_P , $\Delta\chi_S$, and $\Delta\chi_P$.

4.4 Results and discussion

4.4.1 Calibration experiment

The calibration is carried out at $\Delta T_P = 100$ K for helium-neon mixture with mole percentage $\chi = 40, 50$, and 60 %v/v, since the performance of the pump and the flow

resistance of R depends on the gas composition. The result of the calibration experiment is shown in figure 4.10. The experiment was repeated three times, but the variation of the data cannot be recognized in the figure. The performance of the Knudsen pump KP, that is, the pressure difference Δp_P versus the volume flow rate q , is plotted in panel (a). It is clear that Δp_P is a linear function of q , but it depends on the mole percentage χ . The values C_1 and C_2 in (4.5a) can be calculated by the least square approximation as

$$C_1 \text{ (kPa/sccm)} = \begin{cases} -0.0201 & (\chi = 40 \%) \\ -0.0187 & (50 \%) \\ -0.0164 & (60 \%) \end{cases}, \quad (4.9a)$$

$$C_2 \text{ (kPa/K)} = \begin{cases} 4.09 \times 10^{-2} & (40 \%) \\ 4.21 \times 10^{-2} & (50 \%) \\ 4.27 \times 10^{-2} & (60 \%) \end{cases}. \quad (4.9b)$$

The pressure differences or the gas flow rates of the pump are larger for helium rich gases since helium is smaller than neon (cf. section 4.2.2). These values show that the present device KP induces pressure difference around 4 kPa when there is no gas flow through the device; the maximum flow rate of the pump is 200 – 260 sccm. This flow rate at atmospheric pressure is quite large compared with the Knudsen pumps found in the literature [17, 59, 62, 65]. The pressure difference Δp_S induced by flow resistance R is shown in panel (b). The pressure difference Δp_S is almost exactly proportional to the flow rate q , and its dependency on the gas composition is weaker compared with the data for Knudsen pump shown in panel (a). The value C_3 in (4.5b) is as follows:

$$C_3 \text{ (kPa/sccm)} = \begin{cases} 0.002076 & (\chi = 40 \%) \\ 0.002005 & (50 \%) \\ 0.001922 & (60 \%) \end{cases}.$$

4.4.2 Experiment without heating

The main experiment using the system given in figure 4.6 is explained below. A precision mixture of helium-neon with mole percentage of helium $\chi_0 = 50.1 \%$ (Air Liquid Japan Ltd.) is used to fill the feed gas tank. The pressure in the tank p_T is initially set to a value in the range of 150–200 kPa. The gas components in the feed tank is analyzed using QMS, and the resultant distribution of ion-current is plotted versus the mass to charge ratio m/z in figure 4.11, where the ion-current is proportional to the partial pressure of the corresponding gas. There are two large peaks at $m/z = 4$ and 20, which correspond to helium 4 (atomic weight) and neon 20, respectively. There is also a peak for neon 22, whose natural abundance ratio is around 9%. Other peaks for nitrogen 28 and oxygen 32 are so small that the mole percentage of nitrogen and oxygen, which come from the residual gas in the feed tank, would be negligible. In the subsequent gas analysis, the ion currents for only helium 4 and neon 20 are measured.

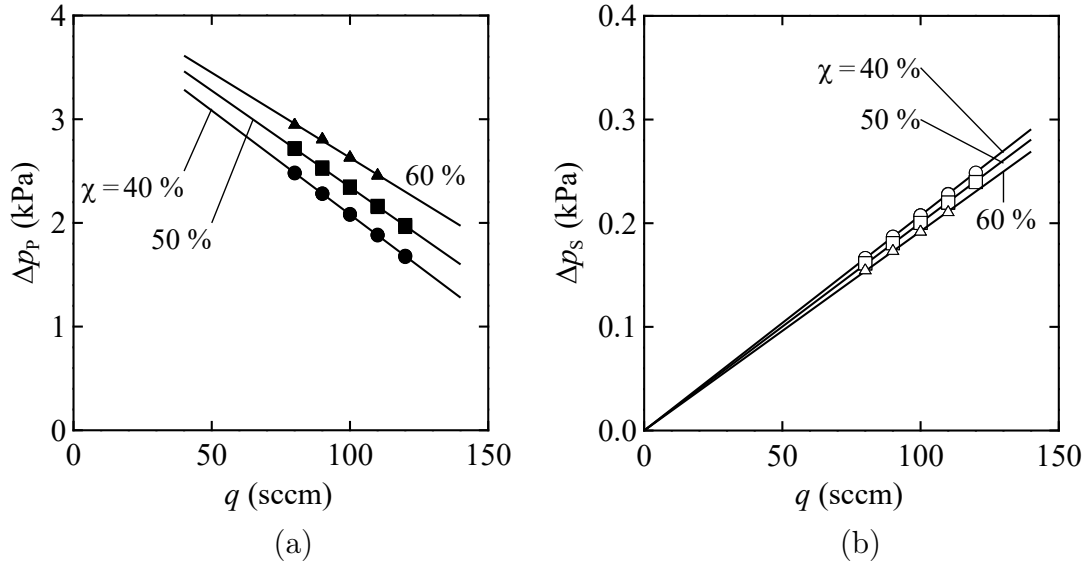


Figure 4.10: Result of calibration experiment for helium-neon mixture. $\circ$, $\bullet$: mole percentage of helium $\chi = 40\%$, $\blacksquare$, $\square$: 50% , and $\blacktriangle$, $\triangle$: 60% . (a) The performance of Knudsen pump KP at $\Delta T_P = 100$ K. The pressure difference Δp_P (kPa) versus the volume flow rate q in sccm. (b) Pressure resistance of R. Δp_S (kPa) versus q (sccm).

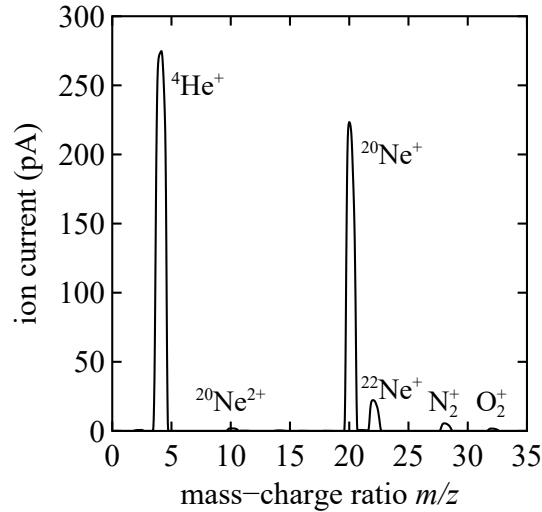


Figure 4.11: Ion-current obtained by the analysis using QMS. The result for the gas in the feed tank sampled from port T in figure 4.6. The abscissa is the mass-charge ratio m/z , and the ordinate is the ion current in pico-ampere.

Table 4.3: Results for the experiment without heating of the Knudsen pumps for $Q_S = Q_P = 0.5$ and 2.5 sccm.

$Q_S (= Q_P)$ (sccm)	0.5 ± 0.02	2.5 ± 0.025
$\Delta\chi_S$ (%)	-0.7	-0.2
$\Delta\chi_P$ (%)	-0.1	0.0
$\Delta\chi_T$ (%)	-0.3	-0.3
ΔT_P (K, for KP1)	0.7	0.8
ΔT_P (K, for KP2)	0.7	0.8
ΔT_S (K)	-0.1	-0.2

Before supplying the power to the Knudsen pumps, an experiment is carried out without temperature differences in the Knudsen pumps KP1, KP2, and KS. Volume flow rates through MS and MP are both set to $Q_S = Q_P = 0.5$ sccm, and the gases are analyzed as follows: (i) sample a gas from port T by sampler G; (ii) measure the ion currents for helium and neon; (iii) dispose the sample gas by the pump attached to G; (iv) the steps (i)–(iii) are repeated seven times to remove the gas in sampler G, dosing value, and related tubings; (v) the steps (i)–(iv) are repeated three times and calculate the gas composition at port T; (vi) the process (i)–(v) is repeated for ports P and S. The gas analysis takes a long time: the process (i)–(v) to measure the gas composition at one port takes around 150 minutes. Therefore, the decrease of the tank pressure p_T possibly become large, which is also shown in the subsequent results as necessary.

The results for the non-heating experiment is summarized in table 4.3. The experiment is carried out for two volume flow rates $Q_S = Q_P = 0.5$ and 2.5 sccm. The temperature differences in pump units ΔT_P (for each units KP1 and KP2) and ΔT_S are below 1 K. The variations of the mole percentages of helium gas $\Delta\chi_S$ and $\Delta\chi_P$ are less than 1 %, and are of similar size with the variation observed near tank $\Delta\chi_T$. This means that the present system does not induce definite variations of the gas composition if the Knudsen pumps are not heated.

4.4.3 Establishment of the molecular exchange state

An example of the result of the process described in section 4.3.2 is plotted in figure 4.12. In this example, the heaters of devices KP1 and KP2 are slightly heated at time $t = 0$ because of the preceding test [figure 4.12(a)]. Therefore, the pump device KP induces slight pressure difference Δp_P [figure 4.12(b)], and a small flow rate is observed [figure 4.12(c)]. The pressure difference Δp_P exceeds 2 kPa in a few minutes by the thermal transpiration flow. The gas flows through the device KS and R as we can see from the positive values of Δp_S and q_S in panels (b) and (c). This process corresponds to $O \rightarrow 1$ in section 4.3.2. It is noted that the value of Δp_S is fairly smaller than that of Δp_P . This means that the flow resistance along the membrane of device KS (e.g., between the ports H1 and H2 on channel H) is quite large. At time $t \approx 5$ (min), the

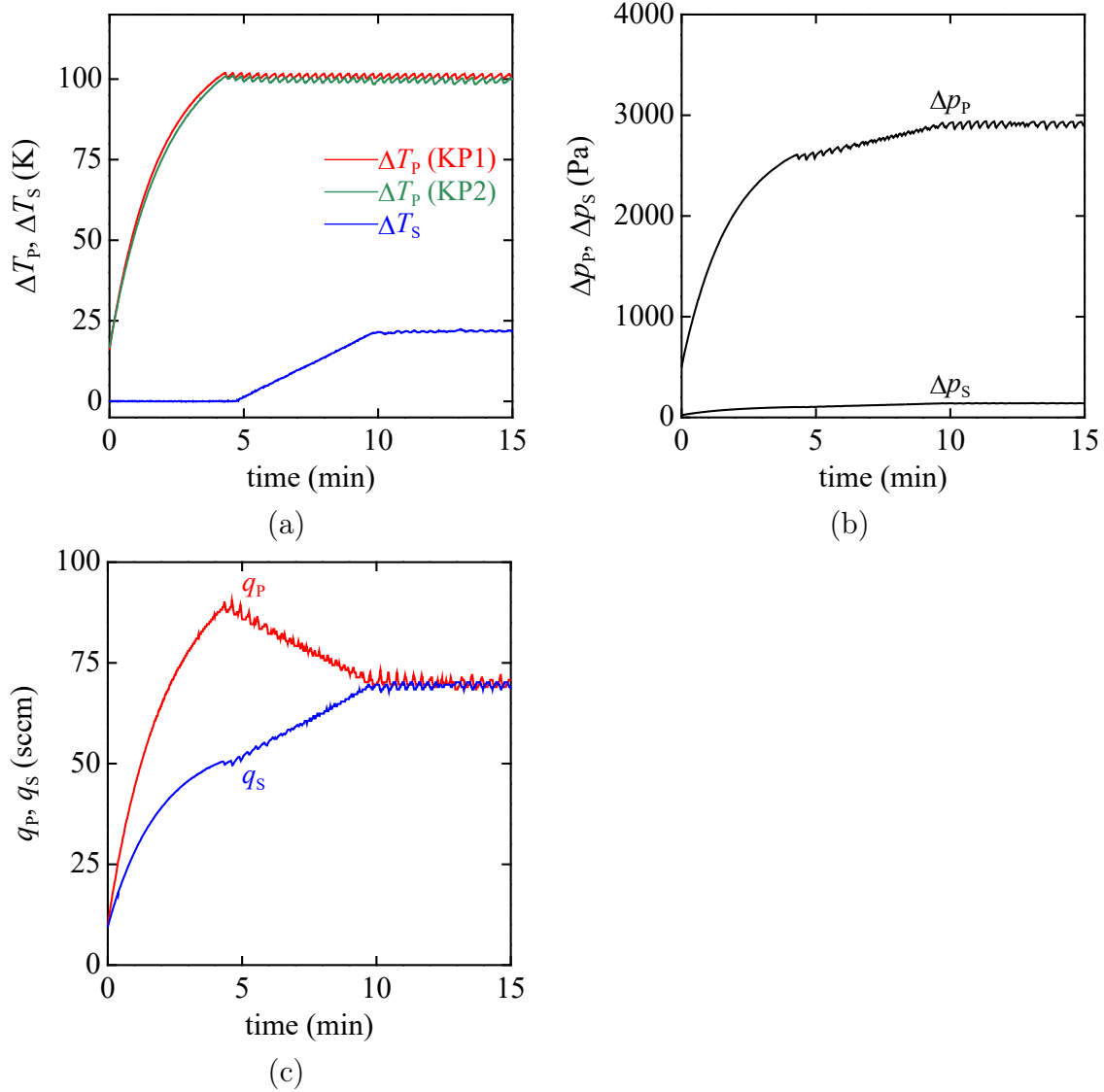


Figure 4.12: An example of the process to establish the molecular exchange state. (a) The temperature difference between the heated and unheated plates of the Knudsen pump. ΔT_P : the values for KP1 and KP2, ΔT_S : KS. (b) The pressure differences Δp_P and Δp_S . (c) The volume flow rates through the system calculated by (4.6a) and (4.6b).

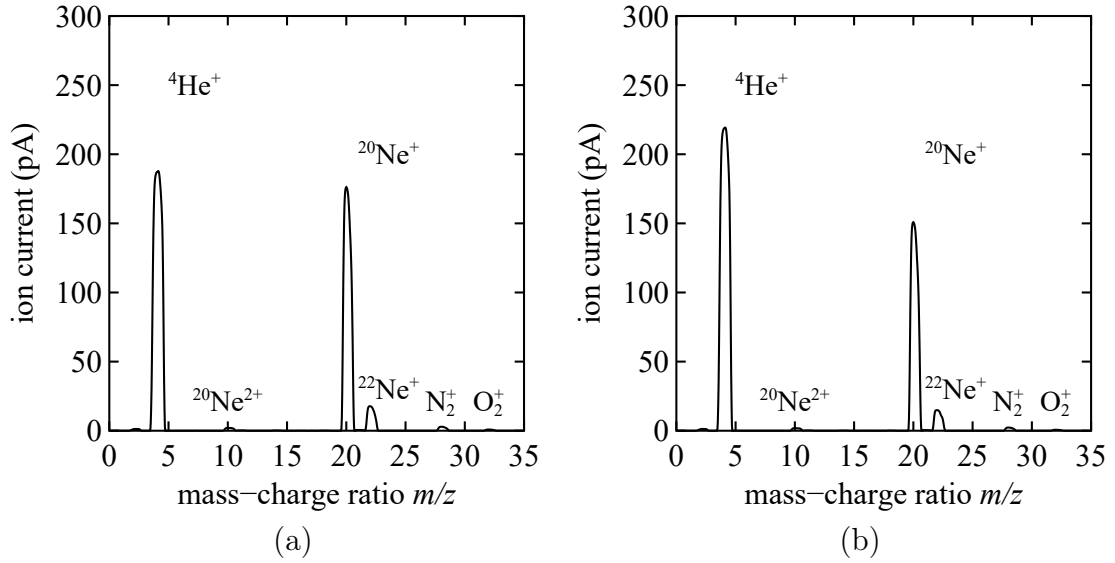


Figure 4.13: Ion-current obtained by the analysis using QMS. An example under the molecular exchange condition (4.7) with $Q_P = Q_S = 5$ sccm. The ion-current versus the mass to charge ratio for the gas sampled from (a) point P and (b) point S.

temperature difference ΔT_P reaches the target value of 100 K. Afterwards, the electricity supplied to KP is controlled to keep $\Delta T_P = 100$ K. The heater in device KS is turned on at this point. As the temperature difference ΔT_S increases, the flow rate q_S through R increases. This process corresponds to $1 \rightarrow 2$ in section 4.3.2. Molecular exchange state (4.7) is established at $t \approx 10$ (min). Afterwards, the temperature difference ΔT_S is regulated to maintain the condition (4.7); ΔT_S is decreased when $q_S > q_P$, and is increased when $q_S < q_P$.

In order to calculate the volume flow rates q_P and q_S using (4.6a) and (4.6b), gas composition at each point P or S is necessary. Although the compositions varies during the start-up process of establishing the molecular exchange state, the values q_P and q_S shown in figure 4.12 are calculated with the mole percentage of feed gas mixture χ_0 . This is because the update interval of the composition is as long as 150 minutes, while the start-up process is completed in 15 minutes.

Figure 4.13 shows ion-current distributions after the molecular exchange condition (4.7) is satisfied under $Q_P = Q_S = 5$ sccm. Panel (a) is the result for the gas at point P. It is clear that the ratio of ion-current of $^{20}\text{Ne}^+$ to that of $^4\text{He}^+$ is larger than the ratio in the feed gas shown in figure 4.11. It means that the gas at point P contains more neon than the feed gas. Conversely, the result for port S [panel (b)] shows that the gas contains more helium than the feed gas. Therefore, the ion-current distributions in figure 4.13 prove that the present separator system works as a gas separator. The mole percentage of helium of the gas at points P and S can be calculated using the mole percentage of the feed gas $\chi_0 = 50.1$ %. The quantitative results on the performance of the gas separator is presented in the next section.

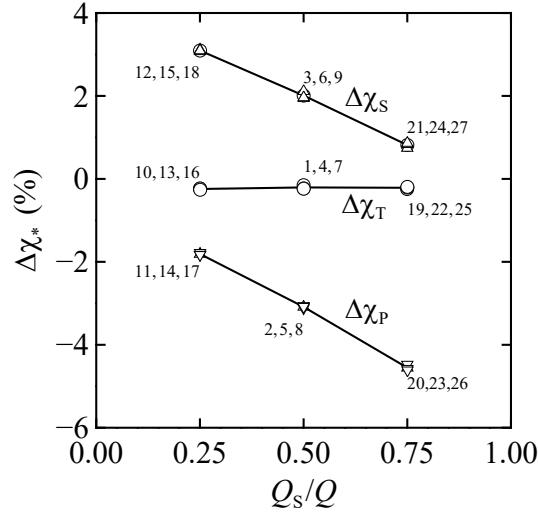


Figure 4.14: The variations of mole percentages $\Delta\chi_*$ from that of the feed tank (mole percentage $\chi_0 = 50.1$ %) at three points $* = S, P$, and T are plotted versus Q_S/Q . Δ : $\Delta\chi_S$, $\circ$: $\Delta\chi_T$, and ∇ : $\Delta\chi_P$. The case for $Q = Q_P + Q_S = 1$ sccm. The numbers near the symbols are the measurement ids.

4.4.4 Gas separation performance

The first performance test is carried out for the cases where helium-neon mixture (mole percentage of helium of the feed gas $\chi_0 = 50.1$ %) is used, the temperature difference of KP ΔT_P is 100 K, and the total flow rate of the product $Q = Q_S + Q_P$ is 1 sccm. The gas compositions at points S, P, and T are measured for three ratios of the product gases $Q_S/Q = 0.25, 0.5$, and 0.75 . The analysis of the gas composition is repeated three times for each port and for each ratio of the product gases. The results of the analyses are identified with the measurement ids which ranges from 1 to 27. The value of Q_S/Q may include the error up to ± 0.03 according to the precision of the mass flow controllers MP and MS.

Figure 4.14 shows the results of the analyses, together with their measurement ids. The abscissa is the ratio Q_S/Q , and the ordinate is the variation of the mole percentage of helium gas from the value χ_0 at the feed tank: $\Delta\chi_*$ ($* = S, P$, and T). For all cases, the gas at point S contains more helium ($\Delta\chi_S > 0$) and the gas at point P contains more neon ($\Delta\chi_P < 0$) compared with the feed mixture. Since the experiment takes almost 24 hours, the tank pressure p_T , which corresponds to the gas pressure in the test system, significantly decreases during the experiment. The variation of p_T is plotted in figure 4.15(a). Although the Knudsen number of the gas in the membrane varies along with the pressure p_T , the measured values of $\Delta\chi_*$ are almost the same over the repeated analyses for each of S, P, or T. The values $\Delta\chi_S$ and $\Delta\chi_P$ decreases similarly as Q_S/Q increases. This means that the amount of helium or neon gas concentrated by the gas separator does not vary with Q_S/Q . The values of $\Delta\chi_F$ estimated using (4.8) are -0.6 % independent of Q_S/Q , which is close to the values at the feed tank $\Delta\chi_T$.

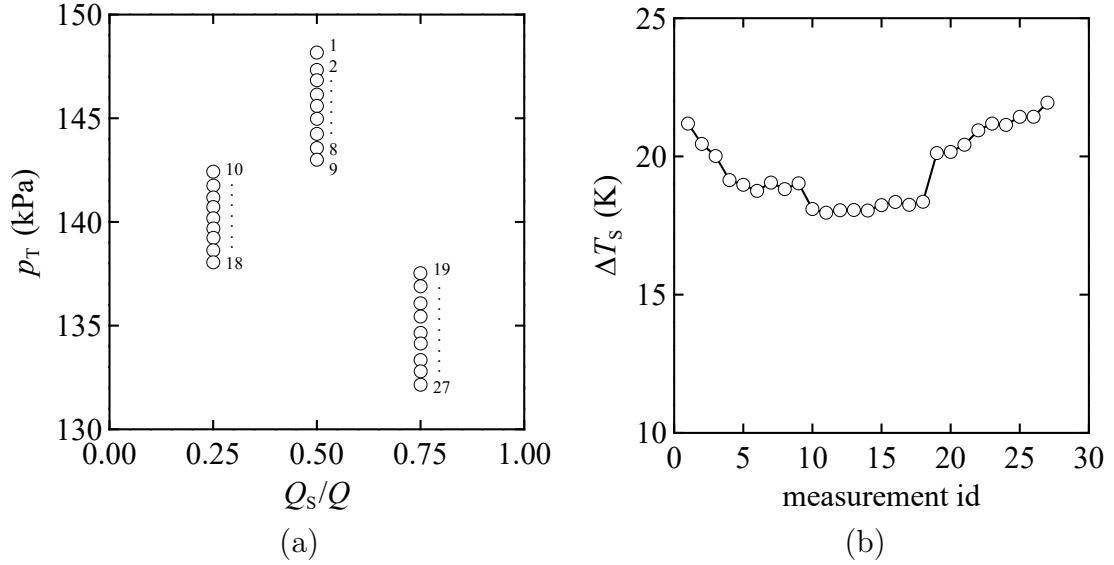


Figure 4.15: (a) The variation of the pressure in the feed tank p_T . The measurement ids are shown in the figure. (b) The variation of the temperature difference ΔT_s in device KS.

Table 4.4: The pressure differences Δp_P and Δp_S , the volume flow rates q_P and q_S , the temperature difference ΔT_P (for KP1 and KP2), and the temperature T_C of the unheated plates C (for devices KP1, KP2, and KS). Each value is averaged over the analysis using QMS for about 150 minutes.

item	min	average	max
Δp_P (Pa)	2907	2921	2931
Δp_S (Pa)	136	138	140
q_P (sccm)	68.2	68.8	69.5
q_S (sccm)	68.0	68.7	69.3
ΔT_P (K, KP1)	100.7	100.9	101.2
ΔT_P (K, KP2)	99.4	99.7	100.0
T_C (K, KP1)	298.9	299.0	299.1
T_C (K, KP2)	300.2	300.3	300.5
T_C (K, KS)	299.7	299.9	300.0

Table 4.5: The variation of the mole percentage of helium at points S, P, and T for various product flow rates $Q = Q_S + Q_P$. The ratio of the product gases $Q_S/Q = 0.5$, and the temperature difference between H and C in the pump unit KP is $\Delta T_P = 100$ K.

Q (sccm)	0.2 ± 0.035	1 ± 0.035	5 ± 0.05
$\Delta\chi_S$ (%)	0.5	2.1 ± 0.08	2.9
$\Delta\chi_P$ (%)	-5.3	-3.0 ± 0.08	-2.7
$\Delta\chi_S - \Delta\chi_P$ (%)	5.8	5.1 ± 0.2	5.6
$\Delta\chi_T$ (%)	0.1	-0.1 ± 0.07	0.1
p_T (kPa)	137	138 – 148	109 – 133
number of measurements	2	7	3

This is the result of the absence of diffusion effect in the feed tubings between T and F for the product flow rate of $Q = 1$ sccm.

The other results of the experiment is summarized in figure 4.15(b) and table 4.4. Each value is averaged over the analysis using QMS for about 150 minutes, and thus the small fluctuation seen in figure 4.12 vanishes. Figure 4.15(b) shows the values of ΔT_S versus the measurement id. The temperature difference takes the values around 20 K, as a result of being controlled to satisfy (4.7). The pressure differences Δp_P and Δp_S , the volume flow rates q_P and q_S , and the temperature differences between H and C plates and the temperature of C plate in Knudsen pump devices (KP1, KP2, and KS) are tabulated in table 4.4 since they are almost constant in 27 measurements.

Next the effect of $Q = Q_S + Q_P$ is investigated. The experiment is carried out for $Q = 0.2, 1$, and 5 sccm, where the ratio of the product gases Q_S/Q is set to 0.5. Table 4.5 gives the values of $\Delta\chi_S$, $\Delta\chi_P$, and $\Delta\chi_T$ obtained by QMS analyses, and the range of the pressure of the tank p_T during the corresponding measurements. The measurements are repeated several times, and the number of measurements are also given in the table. The data shown in figure 4.14 for the case of $Q = 1$ sccm are included in the values of the table so that the standard errors for the case of $Q = 1$ sccm are available. The increase of Q leads a larger variation of the pressure of the tank, and the ranges of the pressure variation is presented in the table.

The values of $\Delta\chi_S - \Delta\chi_P$ in table 4.5 is constant around 5.5 %, while the values $\Delta\chi_S$ and $\Delta\chi_P$ is dependent on Q . The variation of $\Delta\chi_S$ and $\Delta\chi_P$ can be, however, a result of insufficient accuracy of the mass flow controllers: the error in the volume flow rate is around ± 0.018 sccm at $Q_P = Q_S = 0.1$ sccm so that the error in the value of Q_S/Q exceeds 20 %, which may lead fairly large variations of $\Delta\chi_S$ and $\Delta\chi_P$ as expected from figure 4.14. On the contrary, $\Delta\chi_S - \Delta\chi_P$ does not depend much on Q_S/Q in figure 4.14. Therefore, it would be plausible that $\Delta\chi_S - \Delta\chi_P$ in this device does not change much for this range of the product flow rate Q .

4.4.5 Discussion

The results of experiments described in Secs. 4.4.2–4.4.4 demonstrate the feasibility of the present gas separator system. The quantitative feature that the feed mixture is separated into two different gases, one from S is helium-rich and the other from P is neon-rich, is consistent with the results of the numerical simulation [63, 66].

There are, however, several difficulties on the present experiment. The first one is the large flow resistance along the H or C channel in the Knudsen pump device. As seen from figure 4.12(b), the pressure difference between H channel and C channel decreases greatly between the 1-end and 2-end of device KS. There are two causes for this pressure drop. (i) The wire mesh unit used in the present Knudsen pumps; The gas must flow through various mesh or sheets. (ii) The tubings between the Knudsen pumps; The inner diameter of the tubings used in the present gas separator is 1 mm, where the pressure drops significantly for the present circulating flow rate of $q \approx 70$ sccm. As the result, the temperature difference between H and C plates ΔT_S in device KS is limited to about 20 K, which is much smaller than the difference $\Delta T_P = 100$ K in KP. This is quite different from our numerical simulation in [63, 66], where I assumed $\Delta T_P = 90$ K and $\Delta T_S = 60$ K and the variation of mole percentage is mainly obtained by KS. It is possible that the variation of gas composition is primarily caused by the device KP in the present experiment. If the device KP produces a neon-rich gas from port P, the gas from port S must be helium-rich according the mass conservation. However, this cannot be confirmed using the present system where the gas composition can be analyzed only at P, S, or T. One of the solutions is to develop new Knudsen pump with smaller flow resistance along the membrane. In this case, molecular exchange device KS may be composed of multiple Knudsen pumps to induce a larger variation of the gas composition. Another solution would be to compare the gas separation performance of device KP and that of KS. These studies are left to the future works.

Another difficulty is that the variation of mole percentage $\Delta\chi_S - \Delta\chi_P$ is not observed in the range of $0.2 \leq Q$ (sccm) ≤ 10 . If too much product gas is taken out at port S, the amount of helium in channel C of device KS becomes smaller than that in channel H since the product gas at port S is helium-rich. In this case, a difference of mole percentage between channels H and C is induced, which is harmful to the molecular exchange flow. Therefore, it is expected that $\Delta\chi_S - \Delta\chi_P$ decreases for large values of Q . However, the present system where $\Delta\chi_S$ is still small may not sensitive to the size of product flow rate Q . The relation between $\Delta\chi_S - \Delta\chi_P$ and Q will be investigated in the system with larger number of molecular exchange devices KS.

4.5 Conclusion

I have developed and demonstrated a gas separator system composed of two Knudsen pumps with MCE membranes. One of the pumps is used to induce the molecular exchange flow through the membrane, while the other induces the circulating flow in the separator system. The difference of their function is achieved by changing the

temperature difference and the area of the membrane.

The products of the system are two gases whose mole percentages differs about 5.5 % under the total flow rate of 5 sccm for the helium-neon mixture, while the system only uses 27 cm² area of the MCE membrane. Although the flow rates of product gases and the variation of mole percentage are both limited by the area of the membrane in the present work, the significance of the demonstration is ensured by the fact that the flow rate of molecular exchange flow is simply proportional to the area of the membrane in the present gas separation method.

The present study shows that it is possible to make use of the temperature difference not more than 100 K in order to continuously separate a gas mixture into two gases with different composition.

Chapter 5

General Conclusions

In this thesis, the molecular exchange flow is demonstrated for the first time and it is applied to gas separation.

In chapter 2, a device is proposed to demonstrate the molecular exchange flow using a Knudsen pump, which is composed of a porous MCE membrane and one channel along each of the two surfaces of the membrane. A temperature difference and a pressure difference are given between the two surfaces of the membrane to induce the molecular exchange flows, and their effects are accumulated using a flow along the membrane in the device. The performance is estimated theoretically, and then a device is fabricated to be tested for binary mixtures of noble gases.

In the experiment, the gas component of smaller mass of molecules is concentrated, as expected theoretically, at one end of the device to show the feasibility of the molecular exchange flow. The performance of the fabricated device is in qualitatively good agreement with the theoretical result.

In chapter 3, a design of the membrane gas separator using the molecular exchange flow is proposed. The separator system operates by providing a temperature difference as its only energy source. The point is the feature of the Knudsen pump that it can induce the molecular exchange flow as in chapter 2, and it can also pump the gas by the thermal transpiration with larger temperature difference. Connecting multiple Knudsen pumps, the molecular exchange flow induced in some of them can be accumulated by the circulating flow driven by the other pumps.

The proposed design is numerically investigated, and is shown that it can be implemented as a system, in which three Knudsen pumps with same membranes are connected in series: two of them are used to induce the molecular exchange flow, and the other drives the circulating flow in the system. The numerical calculation demonstrates that the gas mixture of neon and argon can be separated into almost pure argon gas and neon gas without any by-products. If the system operates at standard ambient temperature and pressure, the separator is 15 cm long, and the temperature difference is no more than 90 K.

It should be noted that the proposed design is free from the fundamental restriction of the existing methods of membrane gas separation: all component gases permeate in the same direction through membranes.

In chapter 4, a separator system is developed based on the design in the previous chapter. The system composed of two Knudsen pumps with MCE membranes. One of the pumps is used to induce the molecular exchange flow through the membrane, while the other induces the circulating flow in the separator system. The latter operates with a larger temperature difference of 100 K and has a larger area of membrane, compared to the former. It is demonstrated that binary mixtures of gases can be continuously separated into two gases with different composition by means of the molecular exchange flow.

Appendix A

Method of solution of numerical simulation

The pipenet method for the numerical model figure 2.6 is described here. The channel $\#$ ($\# = \text{F, R}$) is sliced into small sections of width $2d$ in X_1 direction. The sections are indexed by i as $\Omega_{\#(i)}$; $i = -L_-/2d$ for the section at $X_1 = -L_-$ and $i = (L + L_+)/2d - 1$ at $X_1 = L + L_+$. We calculate the time-variation of the number of α -molecules in $\Omega_{\#(i)}$ with the mass conservation. For example, we have

$$\frac{2dD}{\kappa T_{\text{F}}} \frac{p_{\text{F}(i)}^{\alpha(k+1)} - p_{\text{F}(i)}^{\alpha(k)}}{\Delta\tau} = D \left(F_{\text{F}(i-1)}^{\alpha(k)} - F_{\text{F}(i)}^{\alpha(k)} \right) + dq_{(i)}^{\alpha(k)} \quad (\alpha = \text{A, B}), \quad (\text{A.1})$$

for the part of channel F over the membrane, where $p_{\text{F}(i)}^{\alpha(k)}$ is the partial pressure of α -gas ($\alpha = \text{A, B}$) in $\Omega_{\text{F}(i)}$ at time $\tau = k\Delta\tau$ ($k = 1, 2, \dots$), $F_{\text{F}(i)}^{\alpha(k)}$ is the molecular flow rate of α -gas from $\Omega_{\text{F}(i)}$ to $\Omega_{\text{F}(i+1)}$ per unit time and per unit area, and $q_{(i)}^{\alpha(k)}$ is that through i -th micro-channel in the direction of $\text{R} \rightarrow \text{F}$. The above formulation can be extended to channel R, and the other parts of channels with no micro-channel. The difference equations for channel F and R in the range of $-L_-/2d + 1 \leq i \leq (L + L_+)/2d - 2$ can be considered as a system of difference equations for $p_{\#(i)}^{\alpha(k)} \left[\# = \text{F, R}; \alpha = \text{A, B}; -L_-/2d \leq i \leq (L + L_+)/2d - 1 \right]$, provided that the flow rates $q_{(i)}^{\alpha(k)}$ and $F_{\#(i)}^{\alpha(k)}$ are expressed by $p_{\#(i)}^{\alpha(k)}$.

Here we discuss on the expression of $q_{(i)}^{\alpha(k)}$. Since the flow in the micro-channel is vanishingly small, the following formula [10–13], which is obtained from the linearized Boltzmann equation, can be used for the molecular flow rate q^α per unit area in a micro-channel:

$$q^\alpha = \bar{n} \sqrt{\frac{2\kappa\bar{T}}{m^\text{A}}} \left[N_T^\alpha \frac{T'}{\bar{T}} + N_p^\alpha \frac{p'}{\bar{p}} + N_x^\alpha \frac{\chi'}{100} \right] d, \quad (\text{A.2})$$

where $\bar{T}$, $\bar{p}$, and $\bar{n}$ ($= \bar{p}/\kappa\bar{T}$) are the representative values of temperature, pressure, and number density, respectively; the values emphasized with prime indicate the corre-

sponding gradients along the micro-channel. N_*^α ($*$ = T , p , and χ) are non-dimensional coefficients that depend on the representative values of Knudsen number $\overline{\text{Kn}}$, mole percentage $\bar{\chi}$, and the parameters in intermolecular potential model including the mass ratio m^B/m^A . These coefficients are to be obtained from separate analysis for thermal transpiration, Poiseuille, and diffusion flows through a long tube [7]. Sharipov et al. clarified overall features of these values by making use of model kinetic equation and Onsager-Casimir reciprocity [10–12]. In [13], a database of these coefficients for various intermolecular potentials has been constructed by around 10^4 cases of numerical calculations of the same kinetic equation and the supplemental asymptotic analysis for small and large Knudsen numbers. The online version of [13] provides a ready-made computer program of the database; we can obtain the values of N_*^α as if they were standard mathematical functions on $\overline{\text{Kn}}$ and $\bar{\chi}$. With the aid of this database, the values of $q_{(i)}^{\alpha(k)}$ are obtained by letting

$$\begin{aligned} T' &\rightarrow \frac{T_F - T_R}{t}, \quad p' \rightarrow \frac{\Delta p_{(i)}^{(k)}}{t}, \quad \chi' \rightarrow \frac{\Delta \chi_{(i)}^{(k)}}{t}, \\ \bar{T} &\rightarrow \frac{T_F + T_R}{2}, \quad \bar{p} \rightarrow \frac{p_{F(i)}^{(k)} + p_{R(i)}^{(k)}}{2}, \quad \bar{\chi} \rightarrow \frac{\chi_{F(i)}^{(k)} + \chi_{R(i)}^{(k)}}{2}, \end{aligned}$$

in (A.2), where $\Delta_{(i)}^{(k)} h$ ($h = \chi, p$) are the difference of mole percentage or pressure between the front and rear side of the membrane

$$\Delta h_{(i)}^{(k)} = h_{F(i)}^{(k)} - h_{R(i)}^{(k)}, \quad (h = \chi, p).$$

The mole percentage $\bar{\chi}$ is computed from the ratio of the partial pressure:

$$\chi_{\#(i)}^{(k)} = \frac{p_{\#(i)}^{A(k)}}{p_{\#(i)}^{(k)}}, \quad p_{\#(i)}^{(k)} = p_{\#(i)}^{A(k)} + p_{\#(i)}^{B(k)} \quad (\# = F, R). \quad (\text{A.3})$$

The value of local Knudsen number of each micro-channel, $\overline{\text{Kn}}$, are calculated according to each intermolecular potential model with the values of $\bar{T}$ and $\bar{p}$ at i -th micro channel.

On the other hand, we have no precise data for $F_{\#(i)}^{\alpha(k)}$: they are non-vanishing fluxes that may affect the mole fraction downstream (that is, they includes the effect of convection terms of fluid dynamic equations), and the channel walls have innumerable holes that may affect flow properties. Here, we assume that they still consist of the part of plane Poiseuille flow proportional to pressure gradient $p' = dp/dX_1$ and the part of diffusion proportional to $\chi' = d\chi/dX_1$, and apply equation (A.2) (with the replacement of d to D) to evaluate $F_{\#(i)}^{\alpha(k)}$ with the aid of finite difference approximation of the derivatives p' and χ' . The coefficient N_p^α for large values of D/d may be replaced with the data by plane Poiseuille flow to save CPU time. The viscosity of the mixture with mole percentage $\bar{\chi}$ is calculated by the data in [13,39,40] with Eqs. (2.2) and (2.3). For hard-sphere mixture with the same diameter of molecules, equation (2.4) with the

replacement of $m^A \rightarrow [\bar{\chi}m^A + (100 - \bar{\chi})m^B]/100$ can be used for the viscosity of the mixture; the maximum error of the viscosity is around $0.3(m^B/m^A - 1)\%$ for $m^B/m^A = 2, 4$, and 10 .

The difference equation (A.1) is of diffusion type, since $F_{\#(i)}^{\alpha(k)}$ is expressed by the difference of $p_{\#(i+1)}^{\alpha(k)}$ and $p_{\#(i)}^{\alpha(k)}$. Therefore we need two boundary conditions for each channel and gas component. These eight conditions are given by (i) total pressures $p = p^A + p^B$ at inlet of F ($p = p_F$) and outlet of R ($p = p_R$), (ii) the value χ_F of mole percentage at inlet of channel F, (iii) two conditions $d\chi/dX_1 = 0$ at the outlets of F and R, (iv) pressure drop p_D between the outlet of F and inlet of R, and (v) the mass conservations for A and B gas between the exit of channel F inlet of channel R. The system of difference equations with above eight boundary conditions determines the distributions of partial pressures $p_{\#(i)}^{\alpha(k+1)}$ $\left[\# = F, R; \alpha = A, B; -L_-/2d \leq i \leq (L + L_+)/2d - 1 \right]$ at time $\tau = \Delta\tau(k+1)$ from those at $\tau = \Delta\tau k$. The process is repeated until we obtain the steady distribution of partial pressures $p_{\#(i)}^{\alpha(k)}$ along channel F and R. Then the distributions of steady mole percentage $\chi_{\#(i)}^{(k)}$ in figure 2.7 are calculated by (A.3). In the numerical calculation, we rewrite explicit form of the difference equation (A.1) for p^α into the implicit form for p^A and p to obtain steady solution quickly with no restriction of CFL condition. In order to reduce the access to the database of N_*^α , the values of $q_{(i)}^{\alpha(k)}$ of M channels nearby are replaced by those of a representative channel.

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List of publications

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