

## Diffusion-Selectivity Analysis of Permanent Gases through Carbon Molecular Sieve Membranes

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**Abstract:** The selectivity of a gas in the carbon molecular sieve membrane (CMSM) can be expressed as the ratio of the product of the diffusivity and the solubility of two different gases. The diffusivity is also expressed as the product of the entropy and the total energy (kinetic and potential energy) in the nano-sized pore of the membrane. The present study calculates the entropic-energy and selectivity of penetrant gases such as H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> from the gas-in-a box theory to physically analyze the diffusivity of penetrant gas in slit-shaped pore of CMSM focusing on the restriction of gas motion based on the size difference between penetrant gas pairs. The contribution of each energy term is converted to entropic term separately. By the conjugated calculation for each entropic-energy, the entropic effects on diffusivity-selectivity for gas pairs such as H<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/N<sub>2</sub>, and O<sub>2</sub>/N<sub>2</sub> were analyzed within active pore of CMSM. In the activated diffusion domain, the calculated value of entropic-selectivity lies between 9.25 and 111.6 for H<sub>2</sub>/N<sub>2</sub>, between 3.36 and 6.0 for CO<sub>2</sub>/N<sub>2</sub>, and between 1.25 and 16.94 for O<sub>2</sub>/N<sub>2</sub>, respectively. The size decrement of active pore in CMSM had the direct effect on the reduction of translational entropic-energy and the contribution of vibrational entropic-energy for N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> was almost negligible. However, the vibrational entropic term of CO<sub>2</sub> might extravagantly affect on the entropic-selectivity.

**Keywords:** nanoporous carbon membrane, activated diffusion, entropic-selectivity, degree of freedom

### 1. Introduction

Activated carbons and molecular sieve carbons are used in many industrial processes such as gas separation, purification and reaction processes. Their properties in such applications depend largely on the geometry, the total volume and the size of pores present in the materials. That is, they depend in particular on the pore size and distribution function. Different precursors, methods of carbonization and activation processes have been intensively investigated by many researchers to produce a large variety of carbon molecular sieve membranes (CMSMs) for gas separation. The active pores of the CMSM are slit-shaped, having

been formed by imperfectly packed microcrystals of graphite, where the size of the opening is distributed over a few angstroms in the matrix[1,2]. In general, the mean pore size of these CMSMs can be similar to or several times bigger than the molecular dimension of the gas penetrant. Sircar et al[3,4]. showed the relationship between the diffusivity of gas and the pore size of CMSM and zeolite characterized as hyper-rigid matrix without the segmental motion of polymer chains. As shown in Figure 1, the key point is that a small change of a few angstroms in the pore diameter can change the gas diffusivity by several orders of magnitude in activated regime. This result gave a valuable ground that the diffusivity of gas was absolutely controlled by the pore size of carbon matrix.

Several years ago, Robeson noted the O<sub>2</sub>/N<sub>2</sub> "upper bound" tradeoff line between gas selectivity and per-

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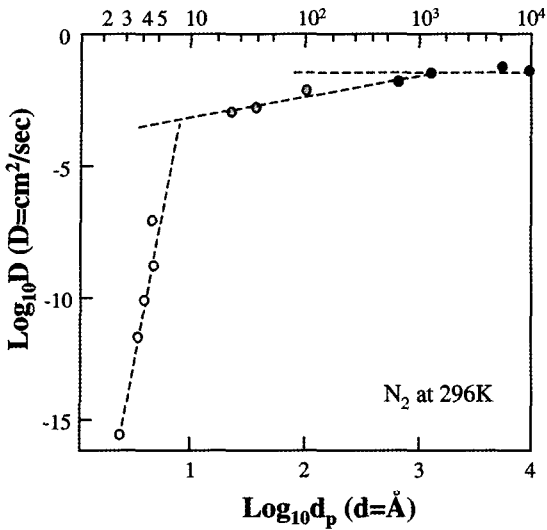


Fig. 1. Gas diffusivity as a function of pore diameter: data taken from [9], respectively. Activation diffusion regime (white circle); Transition diffusion regime (gray circle); Knudsen diffusion regime (dark circle).

meability of polymeric membrane[5]. More recent work has also considered gas transport properties of CMSM, which often exhibited superior gas separation properties compared with traditional flexible polymeric membranes. Previous works by Koros et al[6,7]. reported that the excellent separation properties of CMSM were caused by entropic-selectivity due to the selective reduction of the rotational degree of freedom in the pore of about 3.8 Å (activated diffusion domain) and that the entropic-selectivity of molecular sieving media such as zeolite and CMSM was intrinsically higher than that for a polymer lying on the upper bound tradeoff line as shown in Figure 2.

In order to analyze the diffusivity-selectivity for penetrant gas molecule, the total entropic-energy and selectivity was calculated by gas-in-a box theory based on the statistical and quantum mechanics. We will discuss this matter on the basis of the variation of translational, vibrational, and rotational degree of freedom of penetrant gas due to the restriction of the motion of gas originated from the activated pore dimension of 3.8 Å. The impact of this nano-structural organization on the molecular sieving character of the CMSMs was analyzed in terms of physical separation of each gas mol-

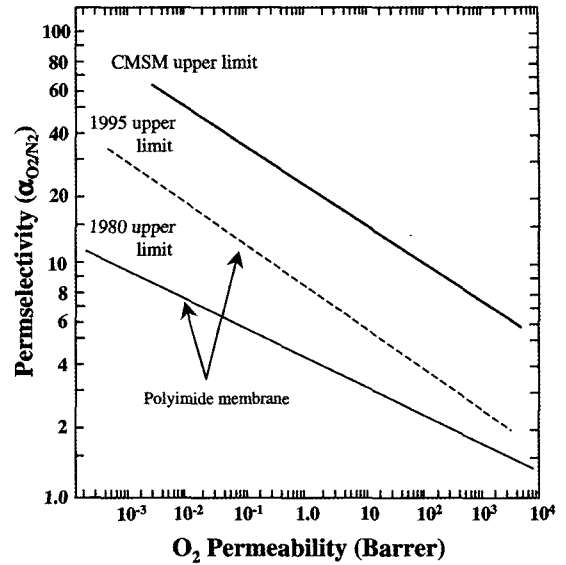


Fig. 2. Tradeoff between permeation and selectivity for  $O_2/N_2$ .

ecule. Also, previously reported experimental diffusivity of Kapton polyimide based CMSM will be analyzed to verify the contribution of entropic-selectivity to diffusivity-selectivity.

## 2. Theory of Gas Permeation

Typically gas permeation through nonporous polymeric membrane, CMSM, and zeolite is followed by the so-called sorption-diffusion mechanism. Permeability of a penetrant,  $P_A$ , calculated as the pressure and thickness normalized flux, is the product of the diffusivity and the solubility,  $D_A$  and  $S_A$ , respectively.

$$P_A = D_A \cdot S_A \quad (1)$$

The diffusivity coefficient is kinetic in nature and is affected by the penetrant size, the chain packing of matrix, and the polymer chain segmental mobility[8]. The sorption coefficient is basically thermodynamic property and depends primarily on the penetrant condensability, the interaction between penetrant and matrix, and the free volume of the matrix.

Membrane separation performance is characterized by the ideal selectivity of a membrane, when the

downstream pressure is negligible. The ideal selectivity,  $\alpha_{A/B}$ , of gas separation membranes can be interpreted as a product of two terms[8].

$$\alpha_{A/B} = \frac{P_A}{P_B} = \left( \frac{D_A}{D_B} \right) \left( \frac{S_A}{S_B} \right) \quad (2)$$

In general, the sorption selectivity, however, of all of the nonporous, polymeric membrane materials for  $O_2/N_2$  separation shows a value between 0.7 and 2, and has relatively lower contribution to selectivity than diffusivity-selectivity[7].

Since diffusion is an activated process in both molecular sieving and polymeric media, the diffusion coefficient can be written as an Arrhenius relationship [9].

$$D = D_0 \exp \left[ -E_d^*/RT \right] \quad (3)$$

where  $E_d^*$  is the energy of activation for the gas molecule to execute a diffusive jump from one cavity to another.  $D_0$  is the temperature-independent preexponential term.  $T$  and  $R$  are the absolute temperature and the universal gas constant, respectively. According to the previous report[10], there is relatively small difference in the exponential energy terms for polymers, zeolites, and CMSMs. Therefore, the preexponential term,  $D_0$ , plays a dominant role in the diffusivity-selectivity. From the Eyring's transition state theory, the preexponential factor can be expressed as the following eq. (4) [8].

$$D_0 = e\lambda^2 \frac{kT}{h} \exp \left[ \frac{S_d^*}{R} \right] \quad (4)$$

where  $\lambda$  is the average diffusive jump length in the diffusion medium,  $S_d^*$  is the activation entropy of diffusion,  $k$  and  $h$  are Boltzman's and Plank's constants, respectively. For the  $O_2/N_2$  and  $CO_2/O_2$  pairs, the difference in the kinetic diameters of two gas molecules is very small. Therefore, the diffusivity-selectivity for such a gas pairs can be given by the following equation.

$$\begin{aligned} \frac{D_A}{D_B} &= \exp \left[ \frac{(S_{DA}^* - S_{DB}^*)}{R} \right] \exp \left[ \frac{-(E_{DA}^* - E_{DB}^*)}{RT} \right] \\ &= \exp \left[ \frac{\Delta S_{A,B}^*}{R} \right] \exp \left[ \frac{-\Delta E_{A,B}^*}{RT} \right] \end{aligned} \quad (5)$$

where  $\Delta E_{A,B}^*$  is the difference in the diffusion activation energy and  $\Delta S_{A,B}^*$  the difference in the diffusion activation entropy for penetrants A and B. The diffusivity-selectivity has been divided into an entropic-selectivity and an energetic-selectivity as shown by eq. (5). The energetic-selectivity is a function of  $\Delta E_{A,B}^*$  while the entropic-selectivity is a function of  $\Delta S_{A,B}^*$ . It was reported [10] that both energetic and entropic factors contribute significantly to the high values of diffusivity-selectivity for CMSM and zeolites, but its contribution to diffusivity-selectivity for the polymeric membranes is negligible.

### 3. Calculation of Entropic-Energy & Selectivity Based on Gas-In-a Box Theory

For many gases, at the temperature that is not too high, the molecular motions or the degree of freedom that must be recognized for the calculation of entropic-energy are those of translation, rotation, and vibration. The entropic-energy of gas molecule consists of the thermal energy and partition functions as presented in the following equation,

$$S = \frac{U_T - U_0}{T} + R \ln \frac{q}{N} + R \quad (6)$$

where  $q$  is total partition functions,  $R$  and  $N$  are the universal gas constant and the Avogadro's constant, respectively.

The value of partition function can be calculated for any particular type of atomic or molecular motion if the energy pattern of the allowed states is known. Fortunately, as for the translational, rotational, and vibrational energies of gas-phase molecules, the pattern is known. The three-dimensional total partition function has the following form and can be separated by the contribution of three kinds of motion to partition

function,

$$q = q_{trans} \cdot q_{vib} \cdot q_{rot} \quad (7)$$

$$\begin{aligned} q_{trans} &= q_x \cdot q_y \cdot q_z \\ &= \frac{\sqrt{\pi}}{2} \left[ \frac{kT}{h^2/8m} \right]^{f/2} \cdot (a)^f = [2\pi mkT/h^2]^{f/2} \cdot (a)^f \end{aligned} \quad (7a)$$

$$q_{vib} = \left[ \frac{1}{1 - e^{-h\nu_{vib}/kT}} \right]^f \quad (7b)$$

$$q_{rot} = \left[ \frac{8\pi^2 I kT}{\sigma h^2} \right]^{\frac{f}{2}} \quad (7c)$$

where  $k$  and  $h$  are Boltzman's and Plank's constants, respectively.  $m$  is the mass of one molecule,  $a$  is one dimensional length (pore diameter), and  $f$  is the degree of freedom.  $\nu_{vib}$ ,  $I$ , and  $\sigma$  are its frequency of vibration, its moment of inertia, and the symmetric number of rotational gas motion, respectively. The thermal energy and partition function for the molecule of an ideal gas can be inserted into eq. (6). The general description of entropic-energy can be expressed as the summation of each contribution for gas motions of the translation, rotation, and vibration.

$$\begin{aligned} S &= S_{trans} + S_{vib} + S_{rot} \\ &= \left[ \frac{(U_T - U_0)_{trans}}{T} + R \ln \frac{q_{trans}}{N} + R \right] \\ &+ \left[ \frac{(U_T - U_0)_{vib}}{T} + R \ln q_{vib} \right] \\ &+ \left[ \frac{(U_T - U_0)_{rot}}{T} + R \ln q_{rot} \right] \end{aligned} \quad (8)$$

The detailed description of each term of the translational, rotational, and vibrational gas motions can be presented by the following equations.

$$\begin{aligned} S_{trans} &= \frac{(U_T - U_0)_{trans}}{T} + R \ln \frac{q_{trans}}{N} + R \\ &= \frac{f/2 \cdot RT}{T} + R \ln \frac{q_{trans}}{N} + R \\ &= R \left\{ \left( \frac{f+2}{2} \right) + \ln \left[ \left( \frac{2\pi mkT}{h^2} \right)^{f/2} \cdot \frac{a^f}{N} \right] \right\} \end{aligned} \quad (9a)$$

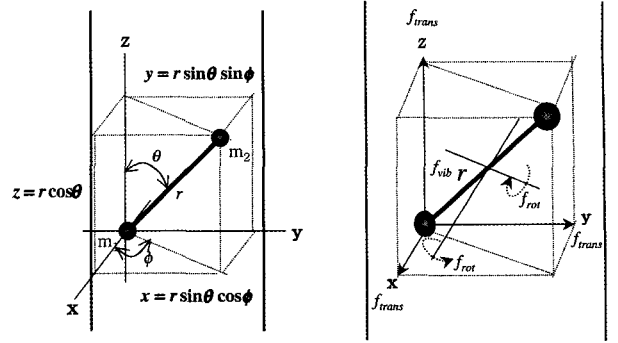


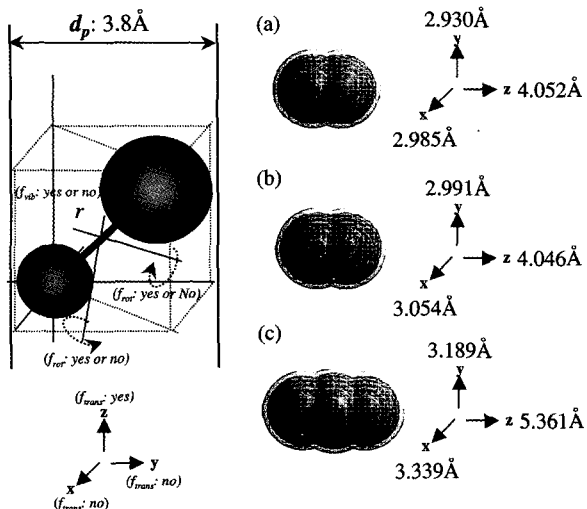
Fig. 3. Cartesian coordinates of a diatomic gas molecule expressed in terms of the interatomic distance  $r$  and the polar angular coordinates  $\theta$  and  $\phi$ .

$$\begin{aligned} S_{vib} &= \frac{(U_T - U_0)_{vib}}{T} + R \ln q_{vib} \\ &= \frac{RT \left[ f \cdot h\nu_{vib}/kT / (e^{(h\nu_{vib}/kT)} - 1) \right]}{T} + R \ln q_{vib} \\ &= R \left[ f \cdot h\nu_{vib}/kT / (e^{(h\nu_{vib}/kT)} - 1) + f \cdot \ln(1/(1 - e^{-(h\nu_{vib}/kT)})) \right] \end{aligned} \quad (9b)$$

$$\begin{aligned} S_{rot} &= \frac{(U_T - U_0)_{rot}}{T} + R \ln q_{rot} \\ &= \frac{RT}{T} + R \ln q_{rot} \\ &= R \left( \frac{f}{2} + \frac{f}{2} \cdot \ln \left( \frac{2IkT}{\sigma h^2} \right) \right) \end{aligned} \quad (9c)$$

The entropic-energy due to the motions of a gas molecule can be represented in terms of motion in each degree of freedom ( $f$ ). As shown in Figure 3, it is possible from eqs. (9a~9c) to calculate the entropic-energy for each of three translational degrees of freedom of a gas molecule related with the allowed energies of the translational motion of a molecule along the three-dimensional Cartesian coordinate. The rotational motion of a linear molecule can be described in terms of rotation around two axes that can be drawn perpendicular to the internuclear axis of the molecule. A linear molecule has two rotational degrees of freedom. The allowed vibrational energies are described for each of the ways that the molecule can vibrate.

A linear diatomic molecule can vibrate only in a single way; it has one vibrational degree of freedom. However, a linear triatomic gas molecule, for example, such as  $\text{CO}_2$  has four modes of vibration (four degrees



**Fig. 4.** Restriction of degree of freedom for gas motions depending on the pore size. (a), (b), and (c) show the x, y, and z-axis dimension of O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> respectively.

of freedom); the dependent stretching mode, an independent symmetric and an anti-symmetric stretching mode, and two perpendicular bending modes[11]. The entropic-energy due to penetrant gas motions according to the degree of freedom of a gas was calculated in the appendix. The entropic-selectivity in eq. (5), therefore, can be analyzed as the summation of the difference of entropic-energies of each mode. The contribution of entropic-selectivity to diffusivity-selectivity can be presented as the exponential function of entropic-energy as expressed in the following eq. (10).

$$\begin{aligned} \exp\left[\frac{\Delta S_{AB}^*}{R}\right] &= \exp\left[\frac{\Delta S_{AB,trans}^* + \Delta S_{AB,vib}^* + \Delta S_{AB,rot}^*}{R}\right] \\ &= \exp\left[\frac{(S_{DA,trans}^* - S_{DB,trans}^*) + (S_{DA,vib}^* - S_{DB,vib}^*) + (S_{DA,rot}^* - S_{DB,rot}^*)}{R}\right] \\ &= \exp\left[\frac{(S_{DA,trans}^* + S_{DA,vib}^* + S_{DA,rot}^*) - (S_{DB,trans}^* + S_{DB,vib}^* + S_{DB,rot}^*)}{R}\right] \end{aligned} \quad (10)$$

#### 4. Restriction of Degree of Freedom of Gas Molecules in CMSM

Knowledge on the dimensions of molecules is essential to understand molecular exclusions as well as the shape of the pore and the size selectivity of CMSM. Figure 4 contains the dimensions of molecules

along the x, y, and z symmetry axes calculated for each atom surrounded by a Van der Waals sphere, without the reaction field correction[12]. The dimension of the penetrant molecule that is critical for entry into pore will depend on the shape of the pore. Specifically, in slit-shaped pores, the minimum dimension of the penetrant molecule should be smaller than that of CMSM, provided that the gas molecules can enter into the pore[12].

The micropores in CMSM are regarded as the slit-shaped[1,2], due to the imperfectly packed microcrystals of graphite, where the size of the openings are similar to the size of penetrant gases such as O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub>, or much bigger than the size of H<sub>2</sub>. Knowing the correlation between CMSM and penetrant molecular dimensions, one can calculate the entropic-energies for translation, vibration, and rotation of a penetrant gas due to the restriction in the motion of gas within active pore of CMSM. Namely, the similarity between the size of gas molecule and the membrane pore provides a clue to the restriction of the degree of freedom of a penetrant gas molecule.

Linear diatomic gas molecules, such as O<sub>2</sub>, N<sub>2</sub>, and H<sub>2</sub>, are considered to have two rotational degrees of freedom due to two axes of symmetry, three translational degrees of freedom in the direction of three axes of Cartesian coordinate, and one vibrational degree of freedom due to the time-dependant variation of inter-nuclear distance between two atoms in a gas molecule. When these molecules pass through the restricted environment of CMSM, O<sub>2</sub> and N<sub>2</sub> molecules can traverse in the only z-direction (diffusion direction) parallel to graphitic planes by losing two translational degrees of freedom. O<sub>2</sub> molecule can pass through the restricted opening rotating about either of the two axes of rotation, but N<sub>2</sub> molecule, which is longer, cannot. N<sub>2</sub> molecule will pass through only if it has given up either one of two rotational degrees of freedom and aligned along its long axis, as previously reported[7]. H<sub>2</sub> molecule, although it passes through the restricted pore window, can maintain its two rotational degrees of freedom, three translational degrees of freedom, and

**Table 1.** Entropic Energy of Each Mode of Penetrant Gas Depending on the Variation of the Degree of Freedom ( $f$ )

Penetrant	$S_{trans}$	$S_{vib}$	$S_{rot}$	
H <sub>2</sub>	$f=1$ 26.9	$f=1$ $2.1 \times 10^{-7}$	$f=1$ 6.5	
	$f=2$ 45.5		$f=2$ 13.0	
	$f=3$ 64.1			
O <sub>2</sub>	$f=1$ 39.4	$f=1$ 0.043	$f=1$ 22.0	
	$f=2$ 71.2		$f=2$ 44.1	
	$f=3$ 102.6			
N <sub>2</sub>	$f=1$ 37.9	$f=1$ $1.6 \times 10^{-3}$	$f=1$ 21.7	
	$f=2$ 67.4		$f=2$ 41.4	
	$f=3$ 97.0			
CO <sub>2</sub>	$f=1$ 39.7	$f=1$ 1.58	$f=1$ 27.5	
	$f=2$ 71.2	$f=2$ 3.16		
	$f=3$ 102.6	$f=3$ 4.74		$f=2$ 54.9
		$f=4$ 6.32		

S unit:  $J/K \cdot mol$ ;  $d_p$ : pore diameter of carbon sieve membrane (calculated with 3.8 Å); 308 K.

one vibrational degree of freedom because its length is much smaller than the pore dimension.

Linear triatomic gas molecule (CO<sub>2</sub>) is considered to have two rotational degrees of freedom due to two axes of symmetry, three translational degrees of freedom in the direction of three axes of Cartesian coordinate, and four vibrational degrees of freedom due to the harmonic or inharmonic variation of two kinds of internuclear distance between two atoms in a gas molecule. CO<sub>2</sub> experiences only a slight decrease in entropy upon entering into the pore due to the reduction of its two translational degrees of freedom or one of two rotational degrees of freedom. As a result of the large reduction of vibrational degree of freedom, CO<sub>2</sub> experiences a large entropic-energy. Consequently, in the slit-shaped pore, the entropic-energy and the entropic-selectivity can be calculated from the probable combination of each mode of degree of freedom.

## 5. Results and Discussion

Several assumptions were introduced to calculate the entropic-energy and the selectivity of penetrant gases in a nano-sized pore of CMSM. First, the pore structure is slip-shaped. Secondly, the entropic-energy

was determined by two parameters, the pore size ( $a$ ) and the degree of freedom ( $f$ ), at constant temperature (308 K). Herein,  $a$  value, factor restricting a dimensional motion of gas, was 3.8 at an activated state. Third, the structure of gas molecule was regarded as a ball-and-spring system.

The entropic-energy in each mode of a penetrant gas depended on the degree of freedom, and was calculated and summarized in Table 1. The translational, vibrational and rotational motions of the linear diatomic molecules (H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub>) have 3, 1 and 2 degrees of freedom, respectively, while those of the linear triatomic molecule (CO<sub>2</sub>) have 3, 4 and 2 degrees of freedom, respectively. These values can be altered by the similarity between the pore dimension of CMSM and the dimension of penetrant gas molecule. As can be seen in Table 1, the entropic-energy for each mode decreased as the gas motion was restricted by the pore size causing the degree of freedom of penetrant gas to change. The calculated result fits very well with the relationship between the disorder for gas motion and the entropy. In addition, the contribution of vibrational entropy is relatively small. Particularly, the entropic-energy for H<sub>2</sub>, O<sub>2</sub>, and N<sub>2</sub> are negligible, i.e., less than 0.043  $J/mol \cdot K$ .

When the gas molecule passes through the pore of the activated diffusion regime, all the gases will experience the reduction of the degree of freedom due to each different restriction of motion. For H<sub>2</sub>/N<sub>2</sub>, O<sub>2</sub>/N<sub>2</sub> and CO<sub>2</sub>/N<sub>2</sub> gas pairs, the entropic-selectivity in activated diffusion regime was calculated for different degree of freedom and summarized in Table 2.

Hydrogen molecule has the minimum dimension of ca. 2 Å whereas nitrogen molecule has a minimum dimension of 2.991 Å. Therefore, there is no restriction of motion in hydrogen molecule. The hydrogen molecule can pass through these pores rotating about either of its axes of rotation ( $f_{rot}=2:2R$ ) and vibrating due to the time-dependant variation of internuclear distance between two atoms in hydrogen molecule ( $f_{vib}=1:1V$ ). On the other hand, the nitrogen molecule may pass through rotating about only one axis. That is, the

**Table 2.** Calculation of Entropic Selectivity with the Degree of Freedom of Gas Molecules in Activated Diffusion Regime

A/B	variation of $f$		$\Delta S(S_A-S_B)$	exp( $\Delta S/R$ )
H <sub>2</sub> /N <sub>2</sub>	(3T,2R,1V)/(1T,1R,1V)	(3T,2R,1V)/(1T,1R,0V)	18.5	9.25
	(3T,2R,1V)/(1T,0R,1V)	(3T,2R,1V)/(1T,0R,0V)	39.2	111.60
CO <sub>2</sub> /N <sub>2</sub>	(1T,1R,4V)/(1T,1R,1V)	(1T,1R,4V)/(1T,1R,0V)	14.9	6.00
	(1T,1R,3V)/(1T,1R,1V)	(1T,1R,3V)/(1T,1R,0V)	13.3	4.95
	(1T,1R,2V)/(1T,1R,1V)	(1T,1R,2V)/(1T,1R,0V)	11.7	4.08
	(1T,1R,1V)/(1T,1R,1V)	(1T,1R,1V)/(1T,1R,0V)	10.1	3.36
O <sub>2</sub> /N <sub>2</sub>	(1T,1R,1V)/(1T,1R,1V)	(1T,1R,1V)/(1T,1R,0V)	1.82	1.25
	(1T,1R,1V)/(1T,0R,1V)	(1T,1R,1V)/(1T,0R,0V)	23.52	16.94

nitrogen molecule may or may not have an additional vibrational ( $f_{vib}=0$  or  $1$ :  $0V$  or  $1V$ ) and rotational degree of freedom ( $f_{rot}=0$  or  $1$ :  $0R$  or  $1R$ ) in the activated pore domain. In this case, hydrogen molecule could transverse to three directions ( $f_{trans}=3$ ,  $3T$ ) even within the graphite plane because the width of the hydrogen molecule was much smaller than the slit width ( $3.8 \text{ \AA}$ , considered in this study). However, nitrogen molecule transversed to only the direction of diffusion with one translational degree of freedom along the graphite plane ( $f_{trans}=1$ ,  $1T$ ). If either of two rotational degrees of freedom was restricted for nitrogen molecule, the entropic-selectivity was calculated to be 9.25 regardless of the variation of vibrational degree of freedom. However, if nitrogen molecule lost all rotational degrees of freedom in pores, which might occur in the case of the slit width being very close to the dimension of the nitrogen molecule, the entropic-selectivity was calculated to be 111.6. This result on H<sub>2</sub>/N<sub>2</sub> analysis shows that the contribution of the vibrational degree of freedom for both gases to entropic-selectivity was negligible, while the restriction of the rotational degree of freedom of nitrogen molecule might markedly affect on the entropic-selectivity for this gas pair.

The x and y dimension of CO<sub>2</sub> are  $3.339 \text{ \AA}$  and  $3.189 \text{ \AA}$ , respectively. Therefore, carbon dioxide molecule has larger minimum dimension than nitrogen molecule. Therefore, it is possible to rotate about one of two axes of rotation while preserving the specific vibrational motion. The carbon dioxide molecule can pass through the pores rotating only one axis of rotation ( $f_{rot}=1$ :  $1R$ )

and vibrating due to the harmonic or inharmonic variation of two internuclear distance between two atoms in carbon dioxide molecule ( $f_{vib}=4 \sim 1$ :  $4V \sim 1V$ ). On the other hand, the nitrogen molecule may or may not have an additional vibrational ( $f_{vib}=1$  or  $0$ :  $1V$  or  $0V$ ) and one rotational degree of freedom ( $f_{rot}=1$ :  $1R$ ) in the activated pore domain assuming the slit-shaped pores. In this case, both carbon dioxide and nitrogen molecules can transverse to the direction of diffusion with one translational degree of freedom along the graphite plane ( $f_{trans}=1$ ,  $1T$ ) because the width of both gas molecules is smaller than the slit width. If either of four vibrational degrees of freedom was gradually restricted for carbon dioxide molecule while losing either of two rotational degrees of freedom for N<sub>2</sub>, the entropic-selectivity was calculated to be in the range of 3.36–6.0 regardless of the variation of vibrational degree of freedom for N<sub>2</sub>. This result on CO<sub>2</sub>/N<sub>2</sub> analysis indicates that the contribution of the vibrational degree of freedom for CO<sub>2</sub> to entropic-selectivity cannot be negligible. Particularly, the restriction of vibrational degree of freedom of CO<sub>2</sub> may mainly affect on the entropic-selectivity for this gas pair.

Oxygen molecule has a similar minimum dimension ( $2.930 \text{ \AA}$ ) with nitrogen molecule. Consequently, the restriction of the motion of oxygen caused by the pore dimension is almost equal to that of nitrogen. However, the restriction of vibrational and rotational degree of freedom is more severe for nitrogen molecule because the x and y dimension of N<sub>2</sub> is relatively larger than O<sub>2</sub> (see Figure 4). The oxygen molecule can pass

**Table 3.** Diffusivity of gas through micropores of carbon molecular sieve membrane derived from Kapton polyimide: data taken from[14]

$D_{H_2}$	$D_{CO_2}$	$D_{N_2}$	$D_{O_2}$	$\alpha(D_{H_2}/D_{N_2})$	$\alpha(D_{O_2}/D_{N_2})$	$\alpha(D_{CO_2}/D_{N_2})$
$1.57 \times 10^{-7}$	$1.13 \times 10^{-10}$	$2.74 \times 10^{-11}$	$5.01 \times 10^{-10}$	$5.7 \times 10^3$	18.2	4.1

D unit:  $cm^2/sec$ ; 308 K

**Table 4.** Contribution of entropic-selectivity to diffusivity-selectivity

A/B	Diffusivity Selectivity <sup>a</sup> $D_A/D_B$	Entropic Selectivity <sup>b</sup> $Exp(\Delta S/R)$	Energetic Selectivity <sup>c</sup> $Exp(-\Delta E/RT)$
$H_2/N_2$	$5.7 \times 10^3$	9.25 ~ 111.6	616.2 ~ 51.0
$O_2/N_2$	18.2	1.25 ~ 16.94	14.5 ~ 1.1
$CO_2/N_2$	4.1	3.36 ~ 6.0	1.22 ~ 0.7

<sup>a</sup> we adopted CMSM based on Kapton polyimide as a model material in order to verify the contribution of entropic selectivity to diffusivity selectivity. Herein, calculated from the experimental results of diffusivity for each penetrant gas. <sup>b</sup> Calculated from the gas-in-a-box theory. <sup>c</sup> Values divided diffusivity selectivity by entropic selectivity. (refer to eq.(2))

through these pores rotating one of two axes for rotation ( $f_{rot}=1$ : 1R) and intrinsically vibrating between two atoms of its molecule ( $f_{vib}=1$ : 1V). On the other hand, the nitrogen molecule may or may not have an additional vibrational ( $f_{vib}=0$  or 1: 0V or 1V) and rotational degree of freedom ( $f_{rot}=0$  or 1: 0R or 1R). In this case, both oxygen and nitrogen molecules transverse to only the direction of diffusion with one translational degree of freedom along the graphite plane ( $f_{trans}=1$ , 1T). If nitrogen molecule serves to restrict one rotational degree of freedom, the entropic-selectivity is calculated to be 1.82 independent of vibrational degree of freedom. However, if nitrogen molecule loses two rotational degrees of freedom in pores, which might occur in the case of the slit width being very close to the width of the nitrogen molecule, the entropic-selectivity is calculated to be 16.94. These values on  $O_2/N_2$  showed a rather broader range than Zimmerman's theoretical result[6] where the entropic-selectivity values lied between 3.7 and 9.0. The rotational degree of freedom for  $N_2$  dominates the entropic-selectivity of this pair.

In summary, the calculated entropic-selectivities lie between 9.25 and 111.6 for  $H_2/N_2$ , between 3.36 and 6.0 for  $CO_2/N_2$ , and between 1.25 and 16.94 for  $O_2/N_2$ , respectively. Therefore, it is possible to analyze that the decrease of several orders of diffusivity with the pore size (see Figure 1) is caused by the remarkable

decrease of entropic-energy due to the restriction of the gas motion. The size decrement of slit-shaped pore in CMSM had a direct impact on the reduction of translational entropic-energy, but the contribution of vibrational entropic-energy was negligible. In addition, the entropic-selectivity in activated diffusion region is higher than that in other regions, such as transitional and Knudsen diffusion regions.

In order to verify the contribution of entropic-selectivity to diffusivity-selectivity, we adopted CMSM based on Kapton polyimide as a model material. The evolution of micropores and the gas permeation properties had been reported on a dense CMSM prepared by pyrolysis of Kapton polyimide film at 1223K under Ar flow[13]. This carbon membrane was investigated in the pore size ranging about 4 Å. The experimental result of diffusivity of pure gases such as hydrogen, carbon dioxide, nitrogen, and oxygen, which will be utilized to analyze of the contribution of entropic-selectivity to diffusivity-selectivity, is presented in Table 3. The diffusivities of gases showed in the order of  $H_2 > O_2 > CO_2 > N_2$  for the carbon membrane based on Kapton polyimide, but its order was not exactly in accordance with the order of minimum dimension of  $CO_2$  (3.189) >  $N_2$  (2.991) >  $O_2$  (2.930) >  $H_2$  (ca. 2), as previously reported by Webster et al. [12] The anomalous behavior that large  $CO_2$  permeated faster than small  $N_2$  may originate from the larger



solubility of CO<sub>2</sub> than that of N<sub>2</sub>.

As presented in Table 4, in the case of H<sub>2</sub>/N<sub>2</sub> gas pair that showed the large difference between the sizes of two gases, the entropic effect on selectivity appears to be remarkable. However, the diffusivity-selectivity was governed entirely by the energetic effect rather than entropic one. For CO<sub>2</sub>/N<sub>2</sub> gas pair, the contribution of entropic-selectivity to diffusivity-selectivity would be expected to be dominant, too. Although the entropic-selectivity for O<sub>2</sub>/N<sub>2</sub> gas pair having the similar size is the smallest, the energetic and entropic effects on selectivity are almost identical. Therefore, from these results, the fact that the higher diffusivity-selectivity of CMSMs was higher than those of the general flexible polymer membrane could be understood based on the structural singularity of CMSMs such as rigidity, pore structure and size etc. causing the increase of entropic-selectivity term.

## 6. Conclusions

H<sub>2</sub>/N<sub>2</sub>, showing the large difference between the sizes of two gases, entropic-selectivity lied between 9.25 and 111.6 in the activated diffusion domain of CMSM. The contribution of the vibrational degree of freedom for both gases to entropic-selectivity was almost negligible from the calculated entropic-energy. The restriction of rotational degree of freedom of nitrogen molecule might mainly affect on the entropic-selectivity. From the analysis of diffusivity for CMSM prepared by pyrolysis of Kapton polyimide, the entropic effect on selectivity appeared to be remarkable, but in this case diffusivity-selectivity would be governed entirely by the energetic effect rather than the entropic one. Also, for CO<sub>2</sub>/N<sub>2</sub>, the entropic-selectivity lied between 3.36 and 6.0. The contribution of the vibrational degree of freedom for carbon dioxide to entropic-selectivity could not be negligible. The restriction of vibrational degree of freedom of CO<sub>2</sub> molecule may extravagantly affect on the entropic-selectivity for this gas pair. The contribution of entropic-selectivity to diffusivity-selectivity would be expected to be dominant

for H<sub>2</sub>/N<sub>2</sub> pair. O<sub>2</sub>/N<sub>2</sub>, which has the similar size, the entropic-selectivity lied between 1.25 and 16.94. The restriction for gas motion contributed to the entropic-selectivity and was governed by the rotational degree of freedom of nitrogen molecule. However, although the entropic-selectivity was the smallest, the entropic effect on selectivity was almost the same as the energetic effect. Therefore, the decrease of several order of diffusivity with the slight decrease of the pore size in activated diffusion regime could be analyzed by the remarkable decrease of entropic-energy due to the restriction of the gas motion. The size decrement of active pores in CMSM had a direct impact on the reduction of translational entropic-energy. The contribution of vibrational entropic energy for N<sub>2</sub>, O<sub>2</sub>, and H<sub>2</sub> (except CO<sub>2</sub>) was almost negligible. In addition, the performance of the high selectivity for CMSM lying on the upper bound tradeoff line could clearly be understood on the basis of the restriction of gas motion by the variation of degree of freedom. Therefore, we could conclude that the physical structure of CMSMs governed the separation of two gas molecules and greatly influenced on the entropic-energy term. This result will be further extended to our new CMSM from polyimidesiloxane precursor[15-18] and will be reported later.

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## Appendix

Partition functions due to each of one-dimensional motion of gas

$$q_{x, trans} (= q_y = q_z) = \sum_0^{\infty} q_i e^{-(\epsilon_i - \epsilon_0)/kT} = \sum_0^{\infty} e^{-(\epsilon_i - \epsilon_0)/kT}$$

$$= \sum_0^{\infty} e^{-(n^2 \cdot h^2/8ma^2)/kT} \approx \int_{n=0}^{n=\infty} e^{-(n^2 \cdot h^2/8ma^2)/kT} dn_x$$

$$= \frac{\sqrt{\pi}}{2} \left[ \frac{kT}{h^2/8ma_x^2} \right]^{1/2}$$

$$q_{vib} = \sum_0^{\infty} q_i e^{-(\epsilon_i - \epsilon_0)/kT} = \sum_0^{\infty} e^{-(\epsilon_i - \epsilon_0)/kT}$$

$$= \sum_0^{\infty} e^{-\left[ \left( v + \frac{1}{2} \right) \frac{h}{2\pi} v_{vib} - \left( \frac{1}{2} \right) \frac{h}{2\pi} v_{vib} \right] / kT}$$

$$\approx \int_{v=0}^{v=\infty} e^{-\left[ \left( v \right) \frac{h}{2\pi} v_{vib} \right] / kT} dv = \left[ \frac{1}{1 - e^{-\frac{1}{h v_{vib}} / kT}} \right]$$

$$q_{rot} = \sum_0^{\infty} q_i e^{-(\epsilon_i - \epsilon_0)/kT} = \sum_0^{\infty} e^{-(\epsilon_i - \epsilon_0)/kT}$$

$$= \sum_0^{\infty} e^{-\left[ J(1+J) \frac{h^2}{2I} \right] / kT}$$

$$\approx \int_{J=0}^{J=\infty} e^{-\left[ J(1+J) \frac{h^2}{2I} \right] / kT} dJ = \left[ \frac{8\pi^2 I kT}{\sigma h^2} \right]^{1/2}$$

Partition functions due to each of three-dimensional motion of gas

$$q_{trans} = q_x \cdot q_y \cdot q_z$$

$$= \frac{\sqrt{\pi}}{2} \left[ \frac{kT}{h^2/8m} \right]^{f/2} \cdot (a)^f = [2\pi mkT/h^2]^{f/2} \cdot (a)^f$$

$$q_{vib} = \left[ \frac{1}{1 - e^{-\frac{1}{h v_{vib}} / kT}} \right]^f$$

$$q_{rot} = \left[ \frac{8\pi^2 I kT}{\sigma h^2} \right]^{f/2}$$

The calculation of entropic-energy due to each motion of gas was carried out by eq. (8). To calculate partition functions and entropic-energies, the following molecular parameters were used.

Penetrant	M (kg)	$\bar{\nu}$ (cm <sup>-1</sup> )	I (10 <sup>-47</sup> kgm <sup>2</sup> )	$\sigma$ Ref.
Hydrogen	0.002	4404	0.46	2 [15]
Oxygen	0.032	1580	19.36	2 [15]
Nitrogen	0.028	2358	14.01	2 [15]
Carbon dioxide	0.044	667, 1388, 2349	71.70	2 [12]

To calculate of vibrational mode,  $h\nu_{vib} = h(\bar{\nu} \times 2.9979 \times 10^{10} \text{cm} \cdot \text{s}^{-1}) = (1.98610 \cdot 10^{-23}) \bar{\nu}$ , where  $\bar{\nu}$  is the vibrational spacing. I values of CO<sub>2</sub> have three different vibrational spacing values. However, the major vibrational spacing was 667 and was utilized to

calculate of vibrational entropy.

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