Chapter 2
Transport Mechanism of Carbon Membranes

2.1 Transport of Gas Through CMSMs

Mass transfer of gas through a porous membrane can involve several processes depending on the pore structure and the solid [1]. There are four different mechanisms for the transport: Poiseuille flow; Knudsen diffusion; partial condensation/capillary diffusion/selective adsorption and molecular sieving [2, 3]. The transport mechanism exhibited by most of carbon membranes is the molecular sieving mechanism as shown in Fig. 2.1. The carbon membranes contain constrictions in the carbon matrix, which approach the molecular dimensions of the absorbing species [4].

In this manner, they are able to separate the gas molecules of similar sizes effectively. According to this mechanism, the separation is caused by passage of smaller molecules of a gas mixture through the pores while the larger molecules are obstructed. It exhibits high selectivity and permeability for the smaller component of a gas mixture [3]. Carbon matrix itself is impervious suggesting that permeation through carbon membranes can be attributed entirely to the pore system which consists of relatively wide openings with narrow constrictions. The openings contribute the major part of the pore volume and are thus responsible for the adsorption capacity, while the constrictions are responsible for the stereoselectivity of pore penetration by host molecules and for the kinetics of penetration [5]. Hence, the diffusivity of gases in carbon molecular sieve may change abruptly depending on the size and the shape of molecules because carbon molecular sieve has pore sizes close to the dimension of gas molecules [6].

Carbon molecular sieve membrane (CMSM) has been identified as a very promising candidate for gas separation, both in terms of separation properties and stability. These molecular sieves are porous solids that contain constrictions of apertures that approach the molecular dimensions of the diffusing gas molecules. At these constrictions, the interaction energy between the molecule and the carbon is comprised of both dispersive and repulsive interactions. When the opening becomes sufficiently small relative to the size of the diffusing molecule, the repulsive forces dominate and the molecule requires activation energy to pass through the constrictions. In this region of activated diffusion, molecules with only slight differences in size can be effectively separated through molecular sieving [7]. Therefore, the mechanism of gas
permeation and uptake through porous solids is closely related to the internal surface area and, dimensions of the pores and to the surface properties of the solid, rather than to its bulk properties of the solid as in the case with polymers [5].

Carbon molecular sieve membranes suitable for gas separation have been prepared by pyrolyzing thermosetting polymers. CMSMs with pore diameter 3–5 Å have ideal separation factors, ranging from 4 to more than 170 for various gas pairs [2]. The permeation characteristics of the molecular sieve carbon membrane can be varied by changing the high temperature treatment parameters [8].

Another transport mechanism of carbon membrane is selective adsorption-surface diffusion mechanism. Adsorption-selective carbon membranes separate non-adsorbable or weakly adsorbable gases (O₂, N₂, CH₄) from adsorbable gases, such as NH₃, SO₂, H₂S and chlorofluorocarbons (CFCs). The difference between the structure of adsorption-selective carbon membranes (ASCMs) and CMSMs is the size of the micropores. ASCMs have a carbon film with micropores slightly larger than CMSMs, probably in the range of 5–7 Å [9]. It is known that the performance of an asymmetric membrane is governed by the structure of the thin active layer [10]. Meanwhile, the great difference between carbon asymmetric membranes and polymeric asymmetric membranes seems to be in the skin layer as shown in Fig. 2.2. In contrast to polymeric membranes, carbon membranes may be considered as a refractory porous solid where the permeants are non-soluble and merely penetrate through the pore system [8]. It is greatly different from the transport mechanism of polymeric membranes—solution-diffusion mechanism. Figure 2.3 shows the solution-diffusion mechanism in the dense layer of a polymeric membrane. Size (diffusivity) and condensability (solubility) selectivity factors interact with polymer to determine which component passes though the membrane faster [11]. However, carbon membrane requires a very fine control of the pore sizes (diameter < 4 Å) and also often requires operation at an elevated temperature in order to provide practically acceptable flux for the membrane thickness may extend to a range of several microns [9]. The influ-
ence of adsorption of permeants on the pore walls has also to be taken into consideration, especially when permeants have relatively high boiling point [8].

### 2.2 Solution-Diffusion Model for Single Gas Transport

The transport through CMSMs is often studied by using the solution (sorption)-diffusion model. Because of simplicity of the model, a brief description is given below for the transport involved in a single gas system.

According to the Fick’s first law

\[
J = -D \frac{dc}{dx} \tag{2.1}
\]

where \( J \) is the gas flux, \( dc/dx \) is the concentration gradient to the direction of gas flow and \( D \) is diffusivity.
When the solubility of gas in the membrane follows the Henry’s law relationship
\[ c = Sp \] (2.2)
where \( c \) is the concentration in the membrane phase, \( p \) is the external pressure and \( S \) is the proportionality constant called solubility.

Combining Eqs. (2.1) and (2.2) and integrating from the feed side to the permeate side of the membrane, we obtain
\[ J = \frac{SD}{l} \Delta p \] (2.3)
where \( l \) is the membrane thickness and \( \Delta p \) is the transmembrane pressure difference.

Permeability is defined as:
\[ P = SD \] (2.4)
Hence,
\[ J = \frac{P}{l} \Delta p \] (2.5)
often \( l \) cannot be measured. Then, \( P/l \), called permeance, is measured instead of permeability.

Permeability, solubility and diffusivity can all be represented by Arrhenius type equations; i.e.
\[ P = P_0 \exp\left(\frac{-E_p}{RT}\right) \] (2.6)
\[ S = S_0 \exp\left(\frac{-\Delta H_s}{RT}\right) \] (2.7)
\[ D = D_0 \exp\left(\frac{-E_d}{RT}\right) \] (2.8)
where \( P_0, S_0 \) and \( D_0 \) are the pre-exponential factor of the respective term. \( R \) and \( T \) are the universal gas constant and the absolute temperature, respectively. \( E_p \) is the activation energy of gas permeation, \( \Delta H_s \) is the heat of solution (sorption) and \( E_d \) is the activation energy for diffusion.

From Eqs. (2.6)–(2.8)
\[ E_p = \Delta H_s + E_d \] (2.9)
usually, \( \Delta H_s \) is negative and \( E_d \) is positive. Therefore, \( E_p \) may be negative or positive, depending on whether solution (sorption) or diffusion governs the transport process.

Sorption does not necessarily follow Henry’s law. For a glassy polymer an assumption is made that there are small cavities in the polymer and the sorption at the
cavities follows Langmuir’s law. Then, the concentration in the membrane is given as the sum of Henry’s law adsorption and Langmuir’s law adsorption

\[ c = k_p p + \frac{c_{h'} b p}{1 + b p} \]  

(2.10)

where \( k_p \) is the Henry’s law constant, \( b \) is the hole affinity constant and \( c_{h'} \) is the saturation constant.

Equation (2.10) is also used to interpret the results from CMSMs. It should be noted that the applicability of solution (sorption)-diffusion model has nothing to do with the presence or absence of the pore.

### 2.3 Solution-Diffusion Model for the Transport of Binary Gas Mixtures

A study by Chen and Yang is described below in detail to show how the transport model is applied for the CMSM [12]. The nomenclature of the original work is retained even though it is different from the one used in Eqs. (2.1)–(2.10). However, analogy in the model development is obvious.

In the study conducted by Chen and Yang, the diffusivities of binary mixtures were measured using the laboratory fabricated CMSM and the results were compared with the authors’ own kinetic theory developed for the prediction of binary diffusivities from pure component diffusivities.

The CMSM was prepared by coating polyfurfuryl alcohol (PFA) on a graphite support followed by pyrolysis. The graphite disk was 4.45 cm in diameter and 0.476 cm in thickness. A thin layer of PFA was coated on one face of the graphite disk. The heating protocol of the coated graphite is as follows: 90°C for 3 h in air; heating to 300°C at 1.5°C/min in \( N_2 \) stream and held at 300°C for 2 h; heating to 500°C at the same heating rate in \( N_2 \) stream and held at 500°C for 6 h. The membrane was then cooled to room temperature. The coating and pyrolysis procedure were repeated 5 times. The thickness of the carbon molecular sieve (CMS) layer was 15 μm.

Equilibrium isotherms of \( CH_4 \) and \( C_2H_6 \) were established by using the gravimetric method, following the weight change of the CMS. The CMS (particles) sample was prepared by pyrolysing PFA according to the same heating protocol but without the graphite substrate. After pyrolysis the the carbonized PFA sample was ground and sieved to 50 mesh for the adsorption experiments.

The diffusivity measurement was made by the diffusion cell. The laboratory prepared CMSM was loaded between two chambers of the diffusion cell. Pure helium (He) gas was fed into the lower chamber (permeate side) while He carrying different concentrations of \( CH_4, C_2H_6 \) or \( CH_4/C_2H_6 \) mixture was fed to the upper chamber (feed side) of the diffusion cell. The pressures on both chambers were kept equal. Hence, the gas transport was solely by the diffusion. From the flow rate and the concentration of the permeant at the outlet of the permeate side stream, the permeant flux can be calculated. The flux measurement was done after waiting for 8 h, at least, to ensure the establishment of the steady state.
Figures 2.4 and 2.5 show the SEM pictures of the laboratory prepared CMSM and the substrate graphite. Figure 2.4 depicts that the CMSM coated on top of the graphite support is crack-free. The thickness of the CMSM layer is 15 µm. Figure 2.5 shows that the surface of the CMSM and the graphite support. The CMSM layer is much smoother with a roughness within 0.02 µm. The pore size in the graphite support is 5–10 µm.

Fig. 2.4 SEM cross-sectional images of (right) CMS layer formed on the surface of graphite substrate, and (left) CMS layer and its surface. (From [12])

Fig. 2.5 SEM images of (left) the surface of CMS layer, and (right) the surface of graphite substrate. (From [12])
The adsorption isotherms for CH$_4$ and C$_2$H$_6$ are given in Figs. 2.6 and 2.7. The data were fitted to the Sippe type isotherm:

$$\frac{q}{q_s} = \frac{bp^n}{1 + bp^n}$$

where $p$ is the gas pressure, $q$ is the amount adsorbed and $q_s$ is the saturated amount adsorbed. $b$ is the Langmuir constant and $n$ is isotherm constant.
Regarding the single component gas diffusion, the flux can be written as:

$$J = -D \frac{\partial q}{\partial x}$$

(2.12)

where $D$ is the diffusivity and $x$ is distance.

Diffusion in molecular sieves is strongly concentration dependent, and is given by:

$$D = \frac{D_0}{1 - (1 - \lambda)\theta}$$

(2.13)

where $\theta$ is the fractional saturation $\theta = q/q_s$, $D_0$ is the diffusivity at zero adsorption and $\lambda$ is an interaction parameter.

At the steady state the gas flux is constant. Then, substituting Eq. (2.13) into Eq. (2.12) and integrating,

$$J = \frac{D_0}{\Delta x (1 - \lambda)} \frac{q_s}{(1 - \lambda)} \ln \left[ \frac{q_s - (1 - \lambda)q_L}{q_s - (1 - \lambda)q_H} \right]$$

(2.14)

where $\Delta x$ is the thickness of CMS layer. The subscripts $H$ and $L$ are for the higher (upper) and lower chamber. Since $q_H \gg q_L$, the equation is further reduced to

$$J = -\frac{D_0}{\Delta x (1 - \lambda)} \frac{q_s}{(1 - \lambda)} \ln \left[ 1 - (1 - \lambda) \frac{bp^n}{1 + bp^n} \right]$$

(2.15)

Table 2.1 shows the parameters involved in Eqs. (2.11) and (2.13) at different temperatures.

When an assumption is made that the diffusivity is not concentration dependent, the flux becomes:

$$J = \frac{D}{\Delta x} \frac{q_s bp^n}{1 + bp^n}$$

(2.15a)

The experimental CH$_4$ and C$_2$H$_6$ fluxes are shown in Figs. 2.8 and 2.9. The symbols are the experimental data. The solid lines are calculated results from Eq. (2.15) using the parameters given in Table 2.1. The broken lines are the best fit data based on

<table>
<thead>
<tr>
<th>Gas</th>
<th>Temperature (K)</th>
<th>$q_s$ (mmol/g)</th>
<th>$b \times 10^4$ (1/Torr)</th>
<th>$n$</th>
<th>$D_0 \times 10^8$ (cm$^2$/s)</th>
<th>$\lambda$</th>
<th>$D \times 10^8$ (cm$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td>297</td>
<td>1.145</td>
<td>4.91</td>
<td>1.24</td>
<td>1.695</td>
<td>0.056</td>
<td>2.379</td>
</tr>
<tr>
<td></td>
<td>323</td>
<td>1.051</td>
<td>4.51</td>
<td>1.21</td>
<td>2.429</td>
<td>0.196</td>
<td>3.047</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>0.797</td>
<td>4.21</td>
<td>1.22</td>
<td>3.428</td>
<td>0.280</td>
<td>4.445</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>297</td>
<td>2.072</td>
<td>20.0</td>
<td>0.84</td>
<td>0.146</td>
<td>0</td>
<td>0.293</td>
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<tr>
<td></td>
<td>323</td>
<td>1.821</td>
<td>53.0</td>
<td>1.03</td>
<td>0.188</td>
<td>0</td>
<td>0.343</td>
</tr>
<tr>
<td></td>
<td>353</td>
<td>1.549</td>
<td>49.4</td>
<td>0.99</td>
<td>0.315</td>
<td>0</td>
<td>0.524</td>
</tr>
</tbody>
</table>
Eq. (2.15a). Equation (2.15) gives better results in fitting than Eq. (2.15a), meaning the effect of concentration on the diffusivity cannot be ignored.

The parameter $\lambda$ defined for a specific molecule A is given as:

$$
\lambda_A = e^{-\left(\varepsilon_{AV} - \varepsilon_{AA}\right)/RT}
$$

(2.16)

$\varepsilon_{AV}$ and $\varepsilon_{AA}$ mean the bond energy of the molecule A and the vacant site and the bond energy of molecule A and the molecule A that already occupied the vacant site, respectively.
In Table 2.1, λ for C\textsubscript{2}H\textsubscript{6} is equal to zero at all temperatures, meaning that ε\textsubscript{AV} is much greater than ε\textsubscript{AA}, while λ for CH\textsubscript{4} decreases with decreasing temperature, meaning that the A–V bonding increases as the temperature decreases.

\( D_0 \), obtained at three temperatures can be given in the form of Arrhenius equation as:

\[ D_0 = D_0^* e^{-E_a/RT} \]  

where \( D_0^* \) is the pre-exponential factor and \( E_a \) is the activation energy of diffusion.

The values for \( D_0^* \) and \( E_a \) are shown in Table 2.2.

For a binary system of components A and B, the fluxes are:

\[ J_A = -D_{AA} \frac{\partial q_A}{\partial x} - D_{AB} \frac{\partial q_B}{\partial x} \]  

\[ J_B = -D_{BA} \frac{\partial q_A}{\partial x} - D_{BB} \frac{\partial q_B}{\partial x} \]  

And the concentration dependent Fickian diffusivities are:

\[ D_{AA} = D_{A0} \left[ \frac{1 - (1 - \lambda_{AB})\theta_B}{1 - (1 - \lambda_A)\theta_A - (1 - \lambda_{AB})\theta_B} \right] \]  

\[ D_{AB} = D_{A0} \left[ \frac{1 - (1 - \lambda_{AB})\theta_A}{1 - (1 - \lambda_A)\theta_A - (1 - \lambda_{AB})\theta_B} \right] \]  

\[ D_{BA} = D_{B0} \left[ \frac{1 - (1 - \lambda_{BA})\theta_B}{1 - (1 - \lambda_B)\theta_B - (1 - \lambda_{BA})\theta_A} \right] \]  

\[ D_{BB} = D_{B0} \left[ \frac{1 - (1 - \lambda_{BA})\theta_A}{1 - (1 - \lambda_B)\theta_B - (1 - \lambda_{BA})\theta_A} \right] \]  

The cross-term \( \lambda_{AB} \) is defined as:

\[ \lambda_{AB} = e^{-(\varepsilon_{AV} - \varepsilon_{AB})/RT} \]  

A similar expression is applicable for \( \lambda_{BA} \).

The cross-term activation energies are given by

\[ \varepsilon_{AB} = \varepsilon_{BA} = (\varepsilon_{AA}\varepsilon_{BB})^{1/2} \]
By substituting the diffusivity Eqs. (2.20)–(2.23) into the flux Eqs. (2.18) and (2.19) and integrating the flux equations over $q_A$ by keeping the other component at a constant average $\bar{q}_B$, the following equations are obtained.

$$J_i = -\frac{1}{\Delta x} \sum_{j=1}^{2} \left[ \tilde{D}_{ij}(\tilde{q}_{jout} - q_{jin}) \right] \quad i = A \text{ and } B$$  \hspace{2cm} (2.26)

where

$$\tilde{D}_{AA} = \frac{1}{q_{Aout} - q_{Ain}} \int_{q_{Ain}}^{q_{Aout}} D_{AA}(q_A \bar{q}_B) dq_A$$  \hspace{2cm} (2.27)

$$\tilde{D}_{AB} = \frac{1}{q_{Bout} - q_{Bin}} \int_{q_{Bin}}^{q_{Bout}} D_{AB}(\bar{q}_A q_B) dq_B$$  \hspace{2cm} (2.28)

Similarly, $\tilde{D}_{BA}$ and $\tilde{D}_{BB}$ can be obtained.

To calculate the $q_s$ for the mixed system adsorbed phase averaging is used

$$\frac{1}{q_s} = \frac{X_A}{q_s A} + \frac{X_B}{q_s B}$$  \hspace{2cm} (2.29)

and

$$\theta_A = \frac{q_A}{q_s}, \theta_B = \frac{q_B}{q_s}, \theta_A + \theta_B \leq 1$$  \hspace{2cm} (2.30)

where $X$ is the adsorbate mole fraction at the equilibrium. To know $q_A$ and $q_B$ for the binary mixture adsorption

$$q_A = \frac{q_s A b_A P^n_A}{1 + b_A P^n_A + b_B P^n_B}$$  \hspace{2cm} (2.31)

is used and similarly for $q_B$.

Finally, for the prediction based on single component system, the following equations are used.

$$J_A = -D_{AA} \frac{dq_A}{dx}$$  \hspace{2cm} (2.32)

$$J_B = -D_{BB} \frac{dq_B}{dx}$$  \hspace{2cm} (2.33)

$$D_{AA} = \frac{D_{A0}}{1 - (1 - \lambda_{AA}) \theta_A}$$  \hspace{2cm} (2.34)
Table 2.3 Comparison of prediction based on the binary system and the single component system

<table>
<thead>
<tr>
<th>Feed gas mole fraction</th>
<th>Experimental flux $\times 10^9$ (mol/cm$^2$s)</th>
<th>Flux predicted, binary theory $\times 10^9$ (mol/cm$^2$s)</th>
<th>Flux predicted, single component $\times 10^9$ (mol/cm$^2$s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{CH}_4$</td>
<td>$\text{C}_2\text{H}_6$</td>
<td>$\text{CH}_4$</td>
</tr>
<tr>
<td>0.611</td>
<td>0.021</td>
<td>18.8</td>
<td>0</td>
</tr>
<tr>
<td>0.138</td>
<td>0.580</td>
<td>3.18</td>
<td>11.6</td>
</tr>
<tr>
<td>0.093</td>
<td>0.430</td>
<td>1.99</td>
<td>9.60</td>
</tr>
<tr>
<td>0.465</td>
<td>0.317</td>
<td>13.6</td>
<td>5.06</td>
</tr>
<tr>
<td>0.349</td>
<td>0.625</td>
<td>8.04</td>
<td>10.4</td>
</tr>
<tr>
<td>0.218</td>
<td>0.125</td>
<td>5.49</td>
<td>2.26</td>
</tr>
</tbody>
</table>

\[ D_{BB} = \frac{D_{B0}}{1 - (1 - \lambda_{BB})\theta_B} \] (2.35)

Table 2.3 shows experimental flux data for the binary system together with predictions based on binary system and single gas component system.

It is obvious from Table 2.3 that prediction based on the binary system produces much better results.

References

Carbon-based Membranes for Separation Processes
Ismail, A.F.; Rana, D.; Matsuura, T.; Foley, H.C.
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