An Integral Fitting Method For Determining Gas Permeability Constant Through Porous Membrane

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ABSTRACT

Although many experiments on membrane reactor use sweep gas for establishing partial pressure, only few works have been dealt with the measurement of permeability constant by using sweep gas. Conventionally, gas permeability constant is determined by the following steps: i) flowing of a single or mixed gas through permeation cell, ii) measuring variables and parameters such as volumetric rate of permeated gas and pressure difference, and iii) solving flux equation using measured variables and parameters to obtain permeability constant. In this study, a method for determining gas permeability constant through porous membrane was developed by fitting experimental and calculated data of binary system. A double cylindrical type of permeation cell with porous membrane as inner tube was used in the experiments, in which two different gases were fed into inlets of the cell (shell and tube sides). Then compositions and volumetric rates of gas exhausting from outlets were measured. Separately, compositions and volumetric rates were also calculated by integrating a set of differential equations derived from species balances in the cell. By using minimization technique, permeability constants were determined when sum of squares of the differences between measured and calculated values reach minimum. This method was tested for determining permeability constants of N2, CO2, and H2 through Vycor glass. At 298 K it was obtained that permeability constants for N2, CO2, and H2 are $2.24 \times 10^{-11}$, $2.23 \times 10^{-11}$ and $6.82 \times 10^{-11}$ mol.s$^{-1}$.m$^{-1}$.Pa$^{-1}$ respectively. Furthermore, experiments and calculations were also conducted for ternary system in which N2 was fed into shell side while mixture of H2/CO2 was fed into tube side. Calculations of ternary system used the constants determined from binary system. Work on ternary system showed that this method has better results than the conventional one.

KEYWORDS: permeability constant, porous membrane, Vycor glass, membrane reactor.
INTRODUCTION

In the efforts to create cleaner production methods, there have been growing research interests on the development of membrane reactor (Armor, 1999; Drioli and Criscuoli, 2000). This reactor can provide higher productivity than conventional reactor due to preferential move of a gas from a reaction mixture. In the operation of membrane reactor, flowing of sweep gas is a common method for facilitating such move since it makes partial pressure difference of the component to be removed across the membrane.

Although many studies on porous membrane reactor use sweep gas for establishing partial pressure, only few works have been dealt with the measurement of permeability constant by using sweep gas. Yet the permeation rate of product or back permeation rate of sweep gas strongly affects the performance of porous membrane reactor (Trianto et. al., 2002). Conventionally gas permeability constant is determined by the following steps: i) flowing of a single or mixed gas through permeation cell in which pressure difference is applied, ii) measuring variables and parameters such as volumetric rate of permeated gas and pressure difference, and iii) solving flux equation using measured variables and parameters to obtain permeability constant. In one conventional method, it requires vacuum pump to vacuuming the permeate side. Another method requires the pressurized feed gas in the feed side. All of these methods require extra equipments or conditions that in many cases are not needed in the membrane reactor experiment with sweep gas.

Itoh et.al. (1988) firstly reported work to measure permeability constants of cyclohexane and benzene in porous Vycor glass by using sweep gas. In this work they used N$_2$ as sweep gas, while cyclohexane or benzene, the species to be determined its permeability constant, was flowed in the feed side. They fitted the measured flow of cyclohexane or benzene in the retentate with the calculated one from model to obtain permeability constant. However, the fitting in their work is only involving one variable, since the permeability constant of N$_2$ was assumed to be already known. Recently, such method was also used to determine permeability constants of isopropyl alcohol and acetone (Trianto et.al., 2001).

The objective of this study is to develop a permeability measurement method based on fitting of measured and calculated values with two unknown variables. Accordingly, two different gases were fed into inlets of the cell (shell and tube sides). The compositions and volumetric rates of gas exhausting from outlets were measured. Separately, compositions and volumetric rates were also calculated by integrating a set of differential equations derived from species balances in the cell. By using minimization technique, permeability constants were determined when sum of squares of the differences between measured and calculated values reach minimum.

1. MODEL

One-dimensional model for analysis of gas transport through cylindrical porous membrane has been developed in the previous papers (Trianto and Kokugan, 2001). It can be written as follows:

Tube side:
\[
\frac{d(f_i^T)}{dz} = \pm \frac{2\pi \Phi_i L_M}{F_{T0} \ln\left(\frac{d_{out}}{d_{in}}\right)} \left(p_i^T - p_i^S\right) \\
\] (1)

Shell side

\[
\frac{d(f_i^S)}{dz} = \pm \frac{2\pi \Phi_i L_M}{F_{T0} \ln\left(\frac{d_{out}}{d_{in}}\right)} \left(p_i^T - p_i^S\right) \\
\] (2)

If a component is removed from a gas mixture, negative sign is used. Otherwise, if a component is added to gas mixture, positive sign is used.

2. EXPERIMENTS AND METHOD

2.1 Experimental Section

Experiments used double cylindrical type of permeation cell with porous Vycor glass (Vycor 7930) as inner tube. Schematic diagram of the apparatus and permeation cell are shown in Fig. 1. It can be seen in the Figure that the apparatus used is a typical arrangement for experiment on membrane reactor operated by sweep gas. For measurement of permeability constant, only two pairs of gas were used, i.e. N2-H2 or N2-CO2. For experiments on ternary system, a mixture of H2-CO2 was flowed in the tube side, while pure N2 was flowed in the shell side. All experiments were conducted co-currently at atmospheric pressure both in the tube and shell side, while temperature was varied from 298 K to 548 K. Calibrated rotameters were used to measure volumetric rate of each gas flowing into permeation cell and bubble-soap flow meters were used to measure volumetric rate of product gases exhausted from permeation cell. Gas chromatography with Porapak-Q column was used to analyze composition of the gas outlets.

2.2. Method

Compositions and volumetric rates were calculated by integrating Equations 1 and 2. ODE solver available in MATLAB 6.5 was used to solve such equations [The MathWorks Home Page]. The initial values, taking H2-N2 system as example, were as follows:

\[
f_{H2}^T = 1; \quad f_{N2}^T = 0; \quad f_{H2}^S = 0; \quad f_{N2}^S = \frac{F_{S0}}{F_{T0}} \text{ at } z = 0 \\
\] (4)

In case of H2-N2 system, F_{S0} and F_{T0} are initial flowrates of N2 and H2 respectively.

All parameters except permeability constants were known. Therefore permeability constants were initially guessed. By using minimization technique, i.e. simplex search method available in MATLAB 6.5, then permeability constants were repeatedly substituted until the sum of squares of the differences between measured and calculated values reach minimum. The sum of squares (FOBJ) to be minimized is:
\[ FOBJ = \sum_i \left( f_{j,i}^T \mid_{\text{meas}} - f_{j,i}^T \mid_{\text{calc}} \right)^2 + \left( f_{j,i}^S \mid_{\text{meas}} - f_{j,i}^S \mid_{\text{calc}} \right)^2 \]  \hspace{1cm} (5)

where \( f_{j,o} \) denotes for dimensionless molar rate in the outlet of permeation cell. The flowchart of this procedure is given in Fig.2.

![Flowchart for fitting experimental and calculated values](image1)

![Fig. 1: Schematic diagram of experimental apparatus and permeation cell](image2)

3. RESULTS AND DISCUSSION
3.1 Results on Permeability Measurement

Fig. 3 shows the permeability constants versus square root of absolute temperature. The values for \( N_2 \) showed in the Fig. 3 are those determined from the experiments on a pair gas of \( CO_2-N_2 \). The values of \( N_2 \) determined by \( H_2-N_2 \) system slightly differ from those determined by \( H_2-CO_2 \) system. The
values of N₂ reported in this paper are the average ones. The deviations from its average values were within 2%. The highest value of H₂ permeability constant through Vycor glass determined in this study was 6.82 x 10⁻¹¹ mol.s⁻¹.m⁻¹.Pa⁻¹ or equivalent to 2.04 x 10⁴ barrer. The reported values of permeability constant through this material spread from 10⁴ – 10⁵ barrer (Falconer et.al., 1995). Therefore it can be said that this method is relatively accurate for determining permeability constant.

According to Fig. 3 almost linearly relationship was obtained. This result is similar with other works, including one of Ferreira-Aparicio et.al (2002). However, when permeability constants were plotted against square root of Molecular Weight of the corresponding species as shown in Fig. 4, a straight line as observed by Ferreira-Aparicio was not obtained. These results suggest that the mechanism that governs flow through porous Vycor glass is not solely due to Knudsen diffusion as reported by Ferreira-Aparicio. Studies conducted by Hwang and Kammermeyer (1975) and Shindo et.al. (1983) revealed the similar phenomenon. Both of works concluded that transport of gases through porous Vycor glass are governed by two types of diffusion, i.e. Knudsen and surface diffusion. Furthermore, deviations from Knudsen diffusion can be determined by comparing the actual separation factor with Knudsen separation factor. At 298 K, the actual separation factors of H₂/N₂ and H₂/CO₂, which are ratios of Φ_H₂/Φ_N₂ and Φ_H₂/Φ_CO₂, are 3.04 and 3.06 respectively. At the same temperature,
Knudsen separation factors of H₂/N₂ and H₂/CO₂ are 3.74 and 4.69 respectively. According to this result, the deviation from Knudsen diffusion for CO₂ is higher than that for N₂.

3.2 Validation using ternary system

To validate the constants thus determined, experiments on ternary system were conducted at temperature of 298 K. In each run of these experiments, a mixture of H₂-CO₂ with known composition was flowed in the tube side, while pure N₂ was flowed in shell side. Calculation was performed using the same variables as used in each run. The permeability constants determined in this work, i.e. by binary experiment, were used in the calculations, and the results were labeled as case #1. For the sake of comparison, calculations were also conducted using permeability constant predicted by Shindo equation, and the results were labeled as case #2.

\[
\Phi \sqrt{MT} = K \left[ \frac{1}{1 + \frac{\beta \varepsilon}{kT}} + \alpha \left\{ \exp \left( \frac{\varepsilon^*}{kT} \right) - 1 \right\} \right]
\]

Table 1 summarizes parameters used for the Shindo equation, while Table 2 compares the permeability constants determined from this work with those predicted by Shindo equation at three different temperatures.

<table>
<thead>
<tr>
<th>Parameters used in Shindo equation</th>
<th>H₂</th>
<th>N₂</th>
<th>CO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>K ×10¹¹ [mol¹/².kg⁻¹/².K¹/².s⁻¹.m⁻¹.Pa⁻¹]</td>
<td>4.01</td>
<td>4.04</td>
<td>4.04</td>
</tr>
<tr>
<td>ε*/k [K]</td>
<td>142</td>
<td>253</td>
<td>390</td>
</tr>
<tr>
<td>M [g.mol⁻¹]</td>
<td>2.0</td>
<td>28.0</td>
<td>44.0</td>
</tr>
<tr>
<td>α</td>
<td>0.246</td>
<td>0.246</td>
<td>0.246</td>
</tr>
<tr>
<td>β</td>
<td>0.606</td>
<td>0.606</td>
<td>0.606</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Case #1</th>
<th>Case #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>Permeability (10⁻¹¹ mol.Pa⁻¹.s⁻¹.m⁻¹)</td>
</tr>
<tr>
<td>H₂</td>
<td>CO₂</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>298</td>
<td>6.82</td>
</tr>
<tr>
<td>348</td>
<td>6.64</td>
</tr>
<tr>
<td>398</td>
<td>6.41</td>
</tr>
</tbody>
</table>

The constants predicted by Shindo equation are based on measurement of single component, and it can be seen in Table 2 that the permeability constants of all three gases determined by this method are higher than those calculated by Shindo equation. Table 3 shows the gas inlet and gas outlet conditions...
measured in the experiments, while Table 4 shows calculation results of gas outlet with the same initial conditions as the experiments for both case #1 and case #2. As it can be seen from Table 4, the calculated results for case #1 gives more accurate value than those for case #2. This suggest that the permeability determination based on this method is appropriate for membrane separation or membrane reactor system operated with sweep gas.

Table 3: Experimental results on ternary system

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Gas Inlet</th>
<th>Gas Outlet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tube</td>
<td>Shell</td>
</tr>
<tr>
<td></td>
<td>Flow [mmol/min]</td>
<td>Composition [%]</td>
</tr>
<tr>
<td>T-75H</td>
<td>H₂ 75 CO₂ 25 N₂ 0</td>
<td>6.264</td>
</tr>
<tr>
<td>T-87H</td>
<td>H₂ 87 CO₂ 13 N₂ 0</td>
<td>6.336</td>
</tr>
</tbody>
</table>

Table 4: Calculated results on ternary system

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Calculated Gas Outlet for Case#1</th>
<th>Calculated Gas Outlet for Case#2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Tube</td>
<td>Shell</td>
</tr>
<tr>
<td></td>
<td>Flow [mmol.min⁻¹]</td>
<td>Composition [%]</td>
</tr>
<tr>
<td>T-75H</td>
<td>H₂ 62.20 CO₂ 25.54 N₂ 12.26</td>
<td>5.354</td>
</tr>
<tr>
<td>T-87H</td>
<td>H₂ 76.73 CO₂ 12.87 N₂ 10.40</td>
<td>5.350</td>
</tr>
</tbody>
</table>

3.3 Effect of ZnO deposition onto membrane surface

As it can be seen in Section 3.2, the permeability constants determined by this method are higher than those determined by Shindo equation. It is important to validate these high values by further investigation, and for the sake of such purpose, permeability constants through a surface-modified Vycor glass were also determined. It was hypothesized that the impregnation will make the constant become lower.
The surface-modified Vycor glass was prepared by impregnating of ZnO onto the Vycor glass surface. A Zn-containing solution was prepared by dissolving nitrate of Zn in distilled water. Then, Vycor glass tube was immersed in the solution, and it was heat up to vaporize the water. The Vycor glass tube then was calcined at 400 °C in 40 ml/min of N₂ stream for 2 hours. The permeability constants were determined according the procedure described previously. The results at 298 K are presented in Table 5. As expected, the permeability constants became lower. However these values are still higher with those predicted by Shindo equation. This suggests that the high values determined by this method are acceptable.

Table 5: Comparison of permeability constants before and after impregnation

<table>
<thead>
<tr>
<th></th>
<th>Before Impregnation</th>
<th>After Impregnation</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>6.82</td>
<td>6.54</td>
</tr>
<tr>
<td>CO₂</td>
<td>2.23</td>
<td>2.05</td>
</tr>
<tr>
<td>N₂</td>
<td>2.24</td>
<td>2.09</td>
</tr>
</tbody>
</table>

4. CONCLUSIONS AND RECOMMENDATIONS

A new method for determining gas permeability constant has been proposed, and it was tested to determine permeability constants of H₂, CO₂ and N₂ through porous Vycor glass membrane. The method offers more simplicity in experiment since it does not require equipments for establishing membrane pressure difference. Although it is simple in experiment, the permeability constants determined from this method are relatively accurate because they are within the range reported by previous works. Furthermore, works on ternary systems showed that this method has better results than conventional one. Experiment on surface-modified Vycor glass showed that the results are acceptable. Due to these reasons it is recommended that this method should be used for membrane permeability testing in the experiment or operation of membrane separation or membrane reactor using porous membrane operated with sweep gas. It is also important to note that the fitting done in this work is still dealt with two variables. Study with more than two variables will be very interesting to know the interaction between species involved.

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Nomenclature:

\( \text{din} \) : inner diameter of membrane, [m]
\( \text{dout} \) : outer diameter of membrane, [m]
\( f \) : dimensionless molar rate, [-]
\( F \) : molar rate, [mol.s⁻¹]
LM : length of membrane, [m]
p : partial pressure, [Pa]
z : dimensionless length, [-]

Greek symbols
Φ : permeability constant, [mol.s⁻¹.m⁻¹.Pa⁻¹]

Subscript:
j : species
O : outlet
S0 : initial components in shell side
T0 : initial components in tube side

Superscript:
S : shell
T : tube

REFERENCES
