Diffusion and Adsorption in porous media

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Introduction

Devices used to Measure Diffusion in Porous Solids

Modes of transport in porous media
  - Knudsen diffusion
  - Viscous flow
  - Continuum diffusion
  - Surface diffusion
Introduction

- Adsorption equilibria is the foremost information that we need to understand an adsorption system.
- To properly design an adsorber, we need to know additional information which is the adsorption kinetics.
- The reason is that most practical solids used in industries are porous and the overall adsorption rate is limited by the ability of adsorbate molecules to diffuse into the particle interior.
- Diffusion processes in porous media and its influence on the overall adsorption rate will be reviewed.
Transport of gases and liquids in capillaries and porous media have significant importance in chemical engineering and can be found in numerous applications, such as:

- capillary rise,
- flow of gases into adsorbents,
- flow of gases into porous catalysts,
- flow of underground water.
Devices used to Measure Diffusion in Porous Solids

- To characterize diffusion in porous media, many experimental devices have been used to determine transport diffusion coefficients.
  - *Graham's System (1830)*
  - *Graham and Loschmidt's Systems (1840)*
  - *Diffusion Cell (1904)*
  - *Hoogschagen's System (1953)*
  - *Stefan Tube (1980)*
Graham's System

- A tube containing gas B is immersed in a water bath with the porous media mounted at the upper end of the tube.
- Gas B diffuses out of the tube and the bulk gas A in the surrounding diffuses into the tube.
- Because the net transport of gas is not zero, the water level inside the tube will either rise or fall.
- If B is heavier, the water level will fall, and if the gas B is lighter the level will rise.
- To maintain constant pressure, Graham adjusted the tube so that the water level inside the tube is always the same as that of the water bath.

He observed that:

\[ \frac{N_A}{N_B} = -\sqrt{\frac{M_B}{M_A}} \]
Graham and Loschmidt's Systems

- Two bulbs are joined together by a tube containing either a porous medium or a capillary.
- Bulbs contain gas A and B have same pressure.
- If gas B is lighter; the molar diffusion flux of A is less than the flux of B, leading the increase in pressure in the left bulb. Due to this increase in pressure, the oil droplet moves to the right, resulting in a balance in the pressures.
- The rate of movement of this oil piston provides the net flux of A and B through the porous plug.
In the diffusion cell configuration, introduced by Buckingham in 1904 and later exploited by Wicke (1940) and Wicke and Kallanbach (1941), gases A and B diffuse across the porous medium.

The flow rates of the two sides can be carefully adjusted to give zero pressure gradient across the media.
Hoogschagen's System

\[ \text{Cu} + \frac{1}{2} \text{O}_2 \xrightarrow{480^\circ\text{C}} \text{CuO} \]

\[ \frac{N_{\text{He}}}{N_{\text{O}_2}} = -\sqrt{\frac{M_{\text{O}_2}}{M_{\text{He}}}} \]
The set up was designed to perform steady state experiments. Binary diffusion of O$_2$ and other gases, such as N$_2$, He and CO$_2$ were used. O$_2$ entering the loop is removed by the copper bed maintained at 480°C. The circulation of gas within the loop is caused by the thermal convection due to the heat generated by the copper bed. The pressure inside the loop is maintained atmospheric by raising or lowering the burette connected to the loop. The flux of the outgoing gas is calculated from the change in the liquid level of the burette, and the incoming oxygen flux is measured by weighing the copper before and after the experiment. The porous plug used was granules in the size range of 1 to 8 microns (give pores much larger than the mean free path at atmospheric pressure).
**Stefan Tube**

- A simple device used by Stefan (Cunningham and Williams, 1980) to study the molecular diffusion or calculate the binary diffusivity.
- The flux of B is given by:

\[
N_B = \frac{P D_{AB}}{L R_g T} \ln \left( \frac{1-p_{B2}/P}{1-p_{B1}/P} \right)
\]

- $p_{B2}$: partial pressure of B at the top of the tube (usually zero if B is removed sufficiently fast by a moving stream of A across the tube),
- $p_{B1}$: partial pressure of B at the liquid gas interface, which is the vapor pressure of B.
- $L$: length of the gas space above the liquid surface to the top of the tube.
- $P$: total pressure
Modes of transport in porous media

- There are basically four modes of transport of molecules inside a capillary or a porous medium:
  - **Free molecular diffusion (Knudsen):** The flow or driving force for the Knudsen diffusion is induced by collision of gaseous molecules with the pore wall of the capillary (that is when the mean free path is greater than the capillary diameter). Therefore, transport of molecules of different type are independent of each other.
  - **Viscous flow (streamline flow):** The flow is driven by a total pressure gradient, and as a result the fluid mixture moves through the capillary without separation because all species move at the same speed.
Continuum diffusion: (Countercurrent flow) This flow is resulting from the collisions among molecules of different type, not of the same type because there is no net momentum change due to the collisions among molecules of the same type. This situation happens when the mean free path is much less than the diameter of the capillary.

Surface diffusion: Different molecules have different mobility on the surface of the capillary due to their different extent of interaction with the surface. Hence a binary mixture can be separated using this type of flow, like the Knudsen diffusion.
# Mean free path

\[ \lambda = \frac{kT}{1.414 P \sigma} \quad \text{[m]} \]

- \( P \) - pressure [ N m\(^{-2} \) ]
- \( k \) - Boltzmann constant (\( = 1.38 \times 10^{-23} \text{ J K}^{-1} \) )
- \( T \) - temperature [ K ]
- \( \sigma \) - collision cross section [ m\(^{2} \) ]

## Table

<table>
<thead>
<tr>
<th>Degree of Vacuum</th>
<th>Pressure (Torr)</th>
<th>Gas Density (molecules m(^{-3} ))</th>
<th>Mean Free Path (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric</td>
<td>760</td>
<td>( 2 \times 10^{25} )</td>
<td>( 7 \times 10^{-8} )</td>
</tr>
<tr>
<td>Low</td>
<td>1</td>
<td>( 3 \times 10^{22} )</td>
<td>( 5 \times 10^{-5} )</td>
</tr>
<tr>
<td>Medium</td>
<td>( 10^{-3} )</td>
<td>( 3 \times 10^{19} )</td>
<td>( 5 \times 10^{-2} )</td>
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<tr>
<td>High</td>
<td>( 10^{-6} )</td>
<td>( 3 \times 10^{16} )</td>
<td>50</td>
</tr>
<tr>
<td>UltraHigh</td>
<td>( 10^{-10} )</td>
<td>( 3 \times 10^{12} )</td>
<td>( 5 \times 10^{5} )</td>
</tr>
</tbody>
</table>
Diffusion through porous media

Modes of transport

- **Knudsen diffusion** \( [D_k = f(d, T^{0.5}, M^{-0.5})] \)
- **Bulk diffusion** \( [D_{AB} = f(T^{1.5}, P^{-1}, M_A^{-0.5}, M_B^{-0.5})] \)
  - Viscous flow \( (D.F. = \Delta P) \)
  - Continuum diffusion (countercurrent diffusive flow of 2 species)
- **Surface diffusion** (flow by its own gradient)

Knudsen number: \( K_n = \frac{\lambda}{d} \)

\( \lambda \) = molecular free path length ; \( d \) = characteristic pore diameter

\( K_n \gg 1 \) Knudsen diffusion ; \( K_n \ll 1 \) Bulk diffusion
Pore size and diffusion regimes

Configurational diffusion
Surface migration
The pore structure of a real solid is so complex that one has to mathematically model the structure.

One of the simplest ways is to assume that the pore structure is a bundle of parallel capillaries running through the medium in the direction of the flow. Therefore, the structural properties of the solid is lumped into transport coefficients or into constants of proportionality.

Let us assume that all capillaries have the same length ($L_c$). Because of random orientation of the capillary, $L_c$ is generally longer than the medium thickness ($L$). A parameter named tortuosity can be defined as:

$$\tau = \frac{L_c}{L} \geq 1$$
In the simplest approach of lumping structure characteristics into transport coefficients, the three parameters characterizing the medium for the three transport mechanisms (bulk, Knudsen, viscous) are:

- The Knudsen flow parameter, $K_0$
- The viscous flow parameter, $B_0$
- The porosity and tortuosity factor, $\varepsilon/q$, for continuum diffusion

For a long circular capillary of radius $r$, these parameters take the following form:

\[
K_0 = \frac{r}{2} \\
B_0 = \frac{r^2}{8} \\
\frac{\varepsilon}{q} = 1 \\
q = \tau^2
\]
Other approaches proposed in the literature are:

- Monte-Carlo simulation,
- Dusty gas model,
- Effective medium theory,
- Periodic capillary model,
- Multiscale approach,
- Percolation model,
- Averaging theorem,
- Random structure model,
- Random capillary structure,
- Stochastic model.
Knudsen diffusion

- The driving force for this transport is the concentration gradient and the parameter characterizing this transport is the so-called Knudsen diffusivity $D_{Ki}$ for the species $i$ or the Knudsen parameter.

- The Knudsen flux depends on the molecular weight of the diffusing species. Molecules with smaller MW travel faster than the ones with higher MW under the same concentration gradient. Thus, separation of mixtures is possible with this mechanism.
Consider transport of molecules through small holes in a thin plate (assures that molecules do not collide with each other).

The flux of species from one side having the molecular density $n$ and vacuum at the other side is given by:

$$J_K = w \, n \, v_T \left[ \frac{\text{molecules}}{\text{cm}^2 \, \text{sec}} \right]$$

Where:

$$v_T = \sqrt{\frac{8k_B T}{\pi m}}$$

- $w$: probability of a molecule pass through the hole, (for long tube $w = 2r/3L$)
- $n$: molecule density (molecule/m$^3$),
- $v_T$: mean thermal molecular speed (m/s)
- $v_T$ = 1250 m/s for He at 298K
- $k_B$: Boltzmann constant (1.38x10$^{-23}$ J/K/molecule),
- $m$: molecular mass.
The flux equation for a very long capillary \((L \gg r)\) is:

\[
J_K = \frac{2r}{3} \sqrt{\frac{8R_g T}{\pi M}} \cdot \frac{\Delta n}{L}
\]

If we define the Knudsen diffusivity as:

\[
D_K = \frac{2}{3} r v_r = \frac{2r}{3} \sqrt{\frac{8R_g T}{\pi M}}
\]

Then, the Knudsen equation can be written in terms of Knudsen diffusivity and the concentration gradient (instead of the integral concentration difference):

\[
J_K = -D_K \frac{dC}{dz} = -D_K \frac{1}{R_g T} \frac{dp}{dz}
\]
At steady state, the Knudsen flux through a capillary is constant.

Integrating eq. with constant conditions at two ends of the capillary, gives:

\[ J_K = \frac{D_K}{R_g T} \frac{\Delta P}{L} = \frac{8}{3} \frac{r}{\sqrt{2\pi M R_g T}} \frac{\Delta P}{L} \]

The proportionality constant is the permeability:

\[ B = \frac{8}{3} \frac{r}{\sqrt{2\pi M R_g T}} \]
Knudsen diffusion in porous medium

- The steady state flux per unit total cross-sectional area of the porous medium is defined as:
  \[ J_K = D_{\text{eff}} \frac{\Delta C}{L} \]

- \( D_{\text{eff}} \) is the effective diffusivity based on the total cross sectional area.

\[
D_{\text{eff}} = \frac{\varepsilon D_K}{(L_c / L)^2} = \frac{\varepsilon D_K}{\tau^2} = \frac{\varepsilon D_K}{q}
\]

\( D_K: \) pore diffusivity

- Thus the Knudsen flux equation for a porous medium is:

\[
J_K = -\frac{\varepsilon D_K}{q} \frac{\partial C}{\partial z} \left[ \frac{\text{mole}}{\text{total area of the porous medium} \cdot \text{time}} \right]
\]
Cont.

- For a porous medium having a pore size distribution $f(r)$:

$$J_K = -\frac{\varepsilon}{\eta} \left[ \int_0^\infty D_K(r) f(r) dr \right] \frac{dC}{dz}$$

- The flow of one species by the Knudsen mechanism is independent of that of the other species.
Graham's Law of Effusion

Consider a system having \( n \) species and each species diffuses according to the Knudsen mechanism. The flux equation in a capillary for the component "\( j \)" is:

\[
J_{K,j} = -D_{K,j} \frac{\partial C_j}{\partial z}
\]

Sum the result for all components gives:

\[
\sum_{j=1}^{N} \frac{J_{K,j}}{D_{K,j}} = - \sum_{j=1}^{N} \frac{dC_j}{dz} = - \frac{d}{dz} \left( \sum_{j=1}^{N} C_j \right) = - \frac{dC}{dz} = - \frac{1}{R_g T} \frac{dP}{dz} = 0
\]
Since Knudsen diffusivity is inversely proportional to the square root of molecular weight, the equation can be written as:

\[ \sum_{j=1}^{N} \sqrt{M_j} J_{K,j} = 0 \]

This is the famous Graham's law of effusion for a multicomponent systems at constant pressure.

For a binary system, the above equation will become:

\[ \frac{J_{K,1}}{J_{K,2}} = -\sqrt{\frac{M_2}{M_1}} \]
Viscous flow

- This mode of transport is due to a total pressure gradient of a continuum fluid mixture. Hence, there is no separation of species due to the viscous flow.

- The driving force is the total pressure gradient and the parameter characterizing the transport is the mixture viscosity, $\mu$, and the viscous flow parameter, $B_0$, which is a function of solid properties only.

- The flow inside the pore is assumed laminar, hence the velocity profile is parabolic in shape.
Viscous Flux in a Capillary

The Poiseuille equation for the volumetric flow rate through a capillary tube of radius $r$ under a pressure gradient $\frac{dP}{dz}$ is:

$$Q = -\frac{\pi r^4}{8\mu} \frac{dP}{dz} = -\frac{\pi d^4}{128\mu} \frac{dP}{dz} \left( \frac{m^3}{\text{sec}} \right)$$

Thus, the molar viscous flux of mixture is obtained by multiplying this volumetric rate with the total molar concentration, $C$, and then dividing the result by the area of the capillary.

$$J_{\text{vis}} = -C \frac{r^2}{8\mu} \frac{dP}{dz} \left( \frac{\text{moles}}{m^2 \text{ - sec}} \right)$$

Where:

$$C = \frac{P}{R_g T}$$

$$J_{\text{vis},i} = x_i J_{\text{vis}}$$
Viscous flux for porous medium

If we assume the solid as a bundle of parallel capillaries of equal diameter and length $L_c$ running through the medium in the direction of flow, the average velocity in the capillary is:

$$u_c = \frac{Q}{\pi r^2} = - \frac{r^2}{8 \mu} \frac{dP}{dz_c}$$

The residence time of the fluid to travel from one end to the other end of the capillary is simply the length of the capillary divided by the average velocity in the capillary:

$$\theta = \frac{L}{v} = \frac{L_c}{u_c}$$
Then, the interstitial velocity of the porous medium is given by:

\[ v = -\frac{r^2}{8\mu} \frac{dP}{dz} \left( \frac{L}{L_c} \right)^2 = -\frac{r^2}{8\mu \tau^2} \frac{dP}{dz} \left( \frac{m}{sec} \right) \]

- \( \tau \) is the tortuosity of the medium.
- The viscous flux in terms of the total cross sectional area is:

\[ J_{vis} = -\left( \frac{B_0}{\mu} \right) \frac{P}{R_g T} \frac{dP}{dz} \left( \frac{moles}{m^2 \cdot sec} \right) \]

\[ B_0 = \frac{\varepsilon r^2}{8\tau^2} \]

\( B_0 \): specific permeability coefficient
Continuum diffusion

Here, the molecule-molecule collision is dominant over the collisions between molecules and the wall.

In this mode of transport, different species move relative to each other.

The parameter characterizing this relative motion between species of different type is the binary diffusion coefficient, $D_{ij}$.

Because of the dependence of this parameter on the collision between molecules, the binary diffusivity is a function of the total pressure and temperature.
The continuum diffusion is more complicated than Knudsen diffusion.

Here, we deal with the diffusion flux of a species within the movement of mixture.

If we choose a moving coordinate system as that moving with the control volume, the diffusion fluxes of species 1 and 2 within that mixture (assuming constant pressure) are given by:

\[ J_{D,1} = -D_{12} \frac{dC_1}{dz} ; \quad J_{D,2} = -D_{21} \frac{dC_2}{dz} \]
As the total fluxes of the two species within the moving coordinate is zero, then:

$$J_{1D} + J_{2D} = 0 = D_{12} \frac{dC_1}{dz} + D_{21} \frac{dC_2}{dz}$$

But $C_1 + C_2 = C$ (constant), the above equation will become:

$$(D_{12} - D_{21})\frac{dC_1}{dz} = 0$$

The necessary requirement is: $D_{12} = D_{21}$

suggesting that the binary diffusivities are symmetric.
The flux equations written with respect to the fixed frame of coordinate are:

\[ N_{D,1} = J_{D,1} + x_1(N_{D,1} + N_{D,2}) \]
\[ N_{D,2} = J_{D,2} + x_2(N_{D,1} + N_{D,2}) \]

For the fluxes with respect to the fixed frame of coordinates:

\[ \frac{N_{D,1}}{N_{D,2}} = -\sqrt{\frac{M_2}{M_1}} \]
Continuum flux in porous medium

For a porous medium, the equivalent flux equation to that for cylindrical capillary is:

\[
\frac{1}{R_g T} \frac{dp_1}{dz} = \frac{x_2 N_{D,1} - x_1 N_{D,2}}{D_{12,\text{eff}}}
\]

where the diffusion flux is based on the total cross sectional area, and the effective diffusivity \(D_{12,\text{eff}}\) is related to the binary diffusivity as follows:

\[
D_{12,\text{eff}} = \frac{\varepsilon}{q} D_{12}
\]
**Binary Diffusivity**

- The equation commonly used to calculate this diffusivity is:

\[
D_{12} = 0.0018583 \sqrt{\frac{T^3 \left( \frac{1}{M_1} + \frac{1}{M_2} \right)}{P \sigma_{12}^2 \Omega_{D,12}}}
\]

- where the binary diffusivity is in cm\(^2\)/sec, total pressure \(P\) is in atm, temperature \(T\) is in K, \(\sigma_{12}\) is the collision diameter in Å, and \(\Omega_{D,12}\) is a dimensionless function of temperature and the intermolecular potential field for one molecule of species 1 and one molecule of species 2.
Surface diffusion

- This mode of transport is the most complicated process among the four mechanisms.
- Surface diffusion is considered as the most important mode of transport for many sorbates as many practical sorbents have high internal surface area.
- We can view the surface as a flat surface with specific sites, at which adsorbed molecules are located.
- Assuming the energy depth of these sites to be larger than the thermal energy of a molecule (kT, where k is the Boltzmann constant), molecules at each site must attain enough energy to move from one site to the next vacant site.
- This is the simple picture of the hopping mechanism, commonly used to describe the surface transport.
Literature data have shown that surface diffusion is important, and the mobility of adsorbed molecules varies with the loading, usually increasing sharply with loading.

Diffusion data for pure gases and their mixtures proved that the extra flow of the gases when the coverage is up to 20% of the monolayer coverage is attributed to the surface diffusion.
Characteristics of Surface Diffusion

- Surface diffusion implies a thermal motion of adsorbed molecules. It should be distinguished from "interstitial" diffusion or intracrystalline diffusion.

- The intracrystalline diffusion is strongly affected by the molecular size and it decreases with an increase in the molecular size. The decrease is much faster than $1/\sqrt{M}$, observed for the case of Knudsen diffusion.

- In contrast to the interstitial diffusion and Knudsen diffusion, the contribution of surface diffusion increases with larger and heavier molecules because these molecules are most easily condensed and adsorbed. This is due to the higher density of adsorbed molecules.
Surface diffusion occurs even at Henry law isotherm.

For microporous solids in many cases the surface flow is significantly higher than gas flow.

Experiments indicated that the surface diffusion in the steady state measurement increases rapidly as the monolayer coverage is approached.

As the monolayer layer is exceeded, the diffusion coefficient shows a minimum and then rises sharply again in the region of capillary condensation.

In general, the measured surface diffusivity shows a nonlinear relationship with surface loading.
Cont.

- It can be divided into three regions: a monolayer region, a multilayer region and a capillary condensation region.
- In the monolayer region which is applicable for most adsorption systems, the effects observed are almost certainly due to surface diffusion.
Flux Equation for surface diffusion

- The flux per unit total cross sectional area of the porous solid in terms of adsorbed phase concentration gradient is:

\[ J_s = -(1 - \varepsilon)D_s \frac{dC_{\mu}}{dx} \text{ mole/m}^2\text{sec} \]

- The surface flux equation in terms of the gradient of gas phase concentration is:

\[ J_s = -(1 - \varepsilon)D_s K \frac{dC}{dz} \]

K: Henry’s law constant
C: gas phase concentration
Temperature Dependence of Surface Diffusivity

- Surface diffusion is an activated process, that is the surface diffusivity follows the Arrhenius equation:

\[ D_s = D_{\infty} \exp(-E_s / R_g T) \]

- The influence of the surface diffusion becomes less important as the temperature increases.

- When temperature is increased, the amount adsorbed on the surface decreases at a rate much faster than the increase in the surface diffusivity, and hence the contribution of the surface flux decreases.
Very often when we deal with diffusion and adsorption system, the total pressure changes with time as well as with distance within a particle due to either the nonequimolar diffusion or as a result of adsorption onto the surface of the particle.

When such situations happen, there will be an additional mechanism for mass transfer: the viscous flow.

The general case happens when bulk diffusion, Knudsen diffusion and viscous flow occur simultaneously within a porous medium (When the system is subject to a pressure variation).

The total flux will be the sum of a flux due to the diffusion mechanism and a flux due to the viscous mechanism.
The flux due to the diffusion mechanism is governed by the modified Stefan-Maxwell equation for the component "i".

\[- \frac{1}{R_g T} \frac{dP_i}{dz} = \sum_{j=1, j\neq i}^{n} y_j N_i^D - y_i N_j^D \frac{N_j^D}{D_{ij}} + \frac{N_i^D}{D_{K,i}}\]

The viscous flux for the component "i" is governed by the Hagen-Poiseuille type equation:

\[N_i^V = -\frac{y_i}{R_g T} \frac{B_0 P}{\mu} \frac{dP}{dz}\]

**P**: total pressure,
**μ**: viscosity of the mixture.
**B_o**: structural parameter of the solid characterizing the viscous flow (=r²/8 for cylindrical pore),

The superscripts "D" and "V" for diffusive and viscous flows.
Dilute systems

- When all species have very low concentration except the \( n \)-th species (the solvent), the modified Stefan-Maxwell equation for component \( i = 1, 2, \ldots, (n-1) \) becomes:

\[
-\frac{1}{R_g T} \frac{dp_i}{dz} \approx \frac{N_i^D}{D_{i,n}} + \frac{N_i^D}{D_{K,i}}
\]

- Solving for this flux contributed by diffusion mechanism, we get:

\[
N_i^D \approx -\frac{D_i^0}{R_g T} \frac{dp_i}{dz}
\]

Where:

\[
\frac{1}{D_i^0} = \frac{1}{D_{K,i}} + \frac{1}{D_{i,n}}
\]
Knudsen Diffusion Control

- When the pore size is very small or the pressure is very low, the mean free path is larger than the size of the pore. In such cases the Knudsen diffusion controls the transport.

- In this case, the Knudsen diffusivity is much smaller than the binary diffusivities $D_{ij}$ as the Knudsen diffusivity is proportional to the pore size while the binary diffusivity is inversely proportional to the total pressure.

- In this case of Knudsen diffusion control, the flux contributed by diffusion is:

$$N_i^D \equiv -\frac{D_{K,i}}{R_g T} \frac{dp_i}{dz}$$
**Bulk Diffusion Control**

- Consider the case whereby the pore is reasonably large and the pressure is high. In this case, the mean free path is much shorter than the pore size, and molecular diffusion will control the transport as the binary diffusivity $D_{ij}$ is much smaller than the Knudsen diffusivity.

- The resulting relation for the flux will be:

$$N_T = -\frac{\sum_{j=1}^{n} \sqrt{M_j} \cdot J_j}{\sum_{j=1}^{n} \sqrt{M_j} \cdot y_j} - \frac{1}{R_g T} \frac{B_0 P}{\mu} \frac{dP}{dz}$$
For pure gas, that is $n = 1$, $y = 1$, the relevant constitutive flux equation is:

$$N_1 = -\frac{1}{R_g T} \left( D_{K,1} + \frac{B_0 P}{\mu_1} \right) \frac{dP}{dz}$$

This simple equation for pure gas gives us a useful tool to study the structure of a porous solid. Making use of information such as the Knudsen diffusivity is proportional to $T^{1/2}$ and inversely proportional to the MW, we can carry out experiments with different gases having different molecular weights and at different temperatures to determine the value for the tortuosity in the Knudsen relation and the viscous parameter $B_o$. 