Effective diffusivity measurements of binary gaseous mixtures with relevance to solid oxide fuel cell anode operation, new method for the interpretation of diffusion data

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Abstract
Effective diffusion coefficients in two porous ceramic materials for a number of binary gas mixtures are determined by using the well-known Wicke-Kallenbach diffusion cell technique. For the calculation of the effective diffusivities from the experimental data, an alternative method is introduced. Parameters of the experimental design rarely considered in such measurements are also examined in order to ensure that for the chosen experimental conditions the assumptions and approximations made are appropriate and valid for the current method. The analysis confirms the validity of the theoretical treatment with which the diffusion data are interpreted. The obtained diffusion results are discussed in the context of the solid oxide fuel cells since the gas pairs used are those relevant to solid oxide fuel cell anode operation.

1. Introduction
Two main designs have been explored in the development of Solid Oxide Fuel Cells; the electrolyte-supported and the electrode-supported. In electrolyte-supported designs, the electrolyte forms a structural element whereas in electrode-supported designs, the electrolyte is deposited as a thin layer on porous support structures and the electrode (anode or cathode) plays the role of the supporting component of the cell [1].

In the electrode-supported designs the ohmic resistance is lower than that in the electrolyte-supported cells because thinner electrolyte films can be employed. As well as lower ohmic resistance, these designs are expected to have the advantage of lower activation polarisation, particularly with the use of the composite electrodes. However the concentration polarisation, especially at high current densities, is expected to be significant.

The concentration polarisation for the anode-supported designs results from the resistance to gas transport through the porous anode and support. In such thick, porous electrodes the fuel supply to the electrolyte is carried out mainly by diffusion of the gaseous species. In addition, the electrode reaction at the electrolyte-anode interface is governed by the diffusion rate of the reactant gas when the current density and the fuel utilisation are high. As the diffusion rates of the reactant gases in the anode are affected by the microstructure of the electrode, the concentration polarisation will in turn depend on the anode specifications (such as the volume percent porosity, the pore size, the tortuosity and the thickness) as a number of studies have shown recently[2-4].

Since the diffusion process is the dominant mode of transport of gaseous species through the porous supported anode, the understanding of the interaction between the gas phase diffusion and the electrode microstructure is of prime importance with regard to the fuel cell performance. The study of gas phase diffusion requires the determination of the gas transport properties and particularly the measurement of the effective diffusion coefficients of gases
relevant to solid oxide fuel cell anode operation. Only when these transport parameters are accurately determined, can losses arising from the diffusion process be quantified.

Several experimental methods have been used for the determination of effective diffusivities of gases in porous catalysts and solids. These established measuring techniques can also be applied to the measurement of binary diffusion coefficients in ceramic porous materials such as the fuel cell support and electrode. They are broadly divided into steady and non-steady state methods. A comparative study of these techniques has been provided by Baiker et al. [5] and by Haines [6].

The widely used steady state method is the steady state diffusion cell first developed by Wicke and Kallenbach [7], and it is used mainly with systems of two gases flowing through a porous medium from one chamber of the diffusion cell to the other. The method is based on steady state counter-current diffusion flux measurement under zero pressure gradient. The overall effective diffusion coefficient is determined from the known dimensions of the pellet, the concentration difference and diffusion rate.

Among the non-steady state methods, pulse response measurements on single pellets [8-10] and in gas chromatographic columns [11] are most widely employed. Each of these methods has its own characteristics and thus effective diffusivity measurements on particular samples do not necessarily yield similar results [5]. The dynamic methods are capable of providing effective diffusivities that account for the macropore as well as the micropore structure of the porous medium and information on the processes taking place within it. Nevertheless, they present the drawbacks of the complex mathematical analysis in order to retrieve information from the obtained data, and of the need for more advanced instrumentation for conducting the diffusion experiments.

On the other hand, the method of the steady state diffusion cell constitutes an easy and a much simpler way to measure diffusion coefficients in porous media. The interpretation of the steady state diffusion measurements is straightforward and the effective diffusivities can be directly calculated by conducting a mass balance in the diffusion cell and applying the appropriate transport equations for diffusion through the porous sample.

In the present work, for the reasons mentioned above, the steady state Wicke-Kallenbach technique was the obvious choice for the measurement of the binary gas diffusion coefficients. The main objective of this study was to measure the effective binary diffusion coefficients of binary gas mixtures relevant to SOFC operation. Moreover an alternative method for the interpretation of the diffusion was also proposed. Parameters of the experimental design rarely considered in such measurements were also evaluated in order to ensure that for the chosen experimental conditions the assumptions and approximations made are appropriate and valid for the current method. The analysis confirmed the validity of the theoretical treatment with which the diffusion data are interpreted.

\section{Theory}

Equation (1) has been commonly used in order to describe, in a binary mixture, the diffusion rate of a gas through a porous sample for the steady state diffusion cell method,

\[ J_A = -\frac{P}{RT} D_{AB}^{eff} \frac{dx_A}{dz} + x_A J_{tot} \]  

with \[ J_{tot} = J_A + J_B \]
where \(J_A\), \(J_B\) (\(kmol/m^2 s\)) are the absolute molar fluxes of species \(A\) and \(B\) respectively, defined with reference to fixed spatial coordinates. The term \(-\frac{P}{RT}D_{AB}^{eff} \frac{dx_A}{dz}\) in Equation (1) is Fick’s first law, which gives the diffusional molar flux for the species \(A\). Note that Fick’s first law gives a local flux defined with respect to the molar average velocity of the mixture.

Integration of Equation (1) at constant pressure conditions for the boundary conditions of \(x_A=x_{A0}\) at \(z=0\) and \(x_A=x_{AL}\) at \(z=L\) yields equation (3) for the diffusional flux of species \(A\),

\[
J_A = -D_{AB}^{eff} \frac{P}{RTL\alpha} \ln \left[ \frac{1-\alpha x_{AL}}{1-\alpha x_{A0}} \right]
\]

with \(\alpha = 1 + J_B/J_A\) and \(L\) being the thickness of the porous medium. It is easy to see that when the mole fraction of the species at the two end surfaces of a porous medium and the flux are measured, the effective diffusivity can be easily obtained.

In describing measurements of steady counterdiffusion, for the study of diffusion of gases in porous catalysts and media, many investigators have assumed equimolar counterdiffusion, that is \(J_A=J_B\). With this assumption, Equation (1) reduces to Fick’s first law (on molar basis). However this condition has not been verified experimentally, since equimolar fluxes have not been observed in experiments involving steady state, binary counterdiffusion. According to Rothfeld [12], the first to consider the fact that the net flux \(J_{net}=J_A+J_B\) was not zero in such experiments was Hoogschagen [13]. Previous workers had assumed (erroneously) that \(J_A+J_B=0\), presumably by analogy with the closed vessel case. However even in a closed volume case and for uniform pressure, it can be shown [14] that there is a net flux contribution to the diffusive flux.

Hoogschagen [13] first observed that the fluxes are inversely proportional to the square roots of the molecular weights,

\[
-J_A/J_B = \left( \frac{M_B}{M_A} \right)^{1/2}.
\]

This observation was explained by Hoogschagen [13,15] in terms of momentum transfer to the walls of the pores. This result was initially considered to hold for the Knudsen range, but it was shown by Dullien and Scott [16] that it also applies to the ordinary diffusion range as well as to the intermediate region. The broad range of validity of this relationship was also reported and confirmed by Hewitt et al [17] in a review of the various phenomena involved in gaseous diffusion in porous media. In all these studies, equation (1) has been used along with the square root relationship, equation (5) to treat the experimentally obtained diffusion data.

An alternative method for treating and processing diffusion data is introduced in this section. It can be shown that this type of experiments under constant pressure and temperature should be analysed assuming equimass counterdiffusion rather than equimolar counterdiffusion, which eventually leads to incorrect results.

Mills [18] examined the true nature of binary diffusion and the implications of a constant pressure on such a system. It was shown that for a system consisting of two vessels or streams of gases connected with a tube, the requirement of the constant pressure results in equimass rather than the equimolar counterdiffusion. Therefore under such conditions, equimolar counterdiffusion fails to describe correctly systems such as that of the steady state diffusion cell and analysis on a molar basis is inappropriate. The theoretical basis for the equimass counterdiffusion is based on the following equation obtained by Mills [18],

\[
\]
\[ J'_{\text{diff}, A} = -\frac{P M_A M_B D_{\text{diff}}^A}{R T [m_A (M_B - M_A) + M_A]} \frac{dm_A}{dz} \]  

(5)

where \( m_A \) is the mass fraction for the species \( A \), \( L \) is the length of the porous medium and \( J'_{\text{diff}, A} \) is the mass diffusion flux \((\text{kg/m}^2 \text{s})\) of species \( A \) relative to the mass average velocity. A similar equation may be written for species \( B \).

Taking as boundary conditions, \( m_A = m_{A0} \) at \( z = 0 \) and \( m_A = m_{AL} \) at \( z = L \), integration of Equation (5) yields for the mass diffusive flux,

\[ \phi = \ln \left[ \frac{m_{AL} (M_B - M_A) + M_A}{m_{A0} (M_B - M_A) + M_A} \right] = -J'_{\text{diff}, B} \]  

(6)

For a constant pressure system, the mass average velocity is zero. This follows from momentum equation (Newton’s second law of motion). A zero mass average velocity means that there is not net contribution (convective flux) to the mass diffusive flux and \( G_A = J'_{\text{diff}, A} \), \( G_B = J'_{\text{diff}, B} \) where \( G_A \) is the absolute mass flux of component \( A \) (relative to stationary coordinate axes) in \( \text{kg/m}^2 \text{s} \).

A limited case is identified for Equation (5) when the two components have identical molecular weights. For instance the gases CO and N\(_2\) have the same molecular weights, molecular shape and size and electronic configuration, that is they are isosteric molecules. In this case the molecular weight for the mixture reduces to \( M = M_A = M_B \) and Equation (5) takes the simple form,

\[ J'_{\text{diff}, A} = -\frac{P D_{\text{diff}}^A M_A}{R T L} \frac{dm_A}{dz} \]  

(7)

Another characteristic of such a case is that the binary diffusion coefficient reduces to the self-diffusion coefficient. Equation (7) is easily integrated for the prescribed boundary conditions and gives a typical linear profile for the mass fraction of component \( A \) across the length \( L \).

In the current work Equation (6) was employed for the calculation for the effective diffusion coefficients of the binary gaseous mixtures in the steady state counterdiffusion experiments.

### 3. Experimental

#### 3.1 Materials and Characterisation Techniques

The porous ceramic materials were calcia stabilised zirconia (CSZ) and magnesia-magnesium aluminate (MMA), and were supplied in the form of approximately 75mm x 75mm x 2mm plates. The CSZ samples had been fired at 1450\(^\circ\)C for one hour and lapped, while the MMA samples had been heated at 1550\(^\circ\)C for one hour and also lapped.

The pore size distributions and the structural properties of the two porous samples were determined by mercury porosimetry. For the CSZ sample analysis, the Hg surface tension was 480.00 \(\text{erg cm}^2\), the Hg contact angle was 130\(^\circ\) and the applied pressure range during the intrusion was from 138.24 \(\text{kPa}\) to 207.04 \(\text{MPa}\). In the MMA analysis the operation parameters were the same, with the applied pressure ranging from 138.10 \(\text{kPa}\) to 206.75 \(\text{MPa}\). In this
work the “PoreMaster® 33000” automated mercury porosimeter of Quantachrome Instruments was used. This pore size analyser achieves a maximum pressure $227.5 \text{ MPa}$ for pore measurements in the range of $440 \mu\text{m}$ to $0.0064 \mu\text{m}$ pore diameter.

### 3.2 Procedure and Apparatus

To apply the Wicke-Kallenbach steady state diffusion cell method for the measurement of the gaseous diffusion coefficients through the porous ceramic materials, a test rig was built, shown in Figure 1. It was designed to provide measured flow rates to each face of the cylindrical sample and to analyse the composition of the inlet and outlet flow streams with a gas chromatograph. The apparatus consisted of the diffusion cell, flow and pressure metering and controlling, equipment and a gas chromatograph along with the data acquisition system.

![Figure 1: Schematic diagram of the apparatus](image)

The main part of the experimental set-up is the diffusion cell. It consisted of a hollow, inner cylindrical chamber, which was designed to hold cylindrical samples up to 13 mm diameter, and which could be employed for steady state as well as dynamic measurements. The samples tested in these experiments had a diameter of 11.7 mm and a thickness of 2 mm. A rubber O-ring supported the sample in the central part of the chamber and a cylindrical barrel sealed the chamber, holding the cylindrical disc in position.

Measurements were performed using nitrogen as the main carrier gas and a range of sample (trace) gases, such as hydrogen, carbon monoxide and methane. This type of gases was selected as relevant to solid oxide fuel cell anode operation. All the gases were supplied by BOC Ltd, (purity 99.998%).

The carrier gas (nitrogen) was fed directly onto the lower end face of the sample at a known flow rate and a mixture of the sample gas and the carrier gas was passed directly along the upper side of the sample, as shown in the schematic of Figure 1. The design of the cell holder was made in such way that the porous sample would sit in an angle of $45^\circ$. That prevented the introduction of the carrier gas and the mixture gas streams directly on the end surfaces of the sample and therefore reduced any errors due to the diffusion resistance in the
gas space on either end of the sample. The direction of gas streams could be regarded as tangential to the sides of the porous sample.

The desired concentration of this mixture stream was obtained by mixing the carrier and the diffusing gas (sample gas) with the aid of a tee-junction, placed downstream. This is indicated as the mixing point in the diagram of Figure 1. The use of the gas mixture fed to one side of the porous sample was necessary to avoid any likely problems arising from use of pure gases such as H₂ and CH₄ (safety reasons) directly into one side of the sample. The flow rates of the inlet gas streams were accurately regulated by thermal-mass flow meters controllers (Bronkhorst Hi-Tech BV) operating at the range from 2 to 100 ml/min.

Pressure difference between the two sides of the sample was eliminated (in practice falling in the range 0-12 Pa) by controlling a needle valve connected at the end of one of the outlet stream lines. The pressure drop was monitored by a high precision differential digital manometer, Digitron 2080P, with an operating range 0-2500 Pa.

In order to maintain a near zero pressure drop across the sample and equal flow rates at both sides of the cell, the two inlet gas streams had to be directed at exactly equal volumetric flow rates. The volumetric flow rates used were 100 and 50 ml/min. The flow rate of 100 ml/min was used for the pair of H₂-N₂. For other binary gas mixtures, the analyses were carried out at 50 ml/min. The latter was dictated by the limitations of the measurement system. In order to obtain detectable amounts of the diffusing gas through the porous sample, lower flow rates had to be employed. The detection of diffusing gases such as CO and CH₄ through the porous sample can only be achieved at lower flow rate because of the lower diffusion rates (small diffusivities) of molecules such as CO and CH₄.

Prior to any diffusion measurements, leak tests were carried out. This type of test involved blank runs in which a solid, impermeable pellet of the same dimensions as the tested porous supports was placed inside the diffusion cell. Ar and N₂ were flowed past the opposite sides of the solid pellet and no measurable flux was detected through it. Therefore the sealing between the sample and the chamber holder, provided by the rubber O-ring, was regarded as being satisfactory.

Samples were taken from both inlet and outlet gas flow streams and analysed with a gas chromatograph (Ai Cambridge Q94 GC), which was configured with a thermal conductivity detector (TCD) and a flame ionisation detector (FID). The output signals from these detectors were recorded by the data acquisition system (JCL 6000 for Windows Chromatography Data system). All the experimental operating conditions such as temperature, pressure and flow rates were also recorded. Measurements were made in the temperature range of 23-27°C and 1 atm total pressure.

Steady state diffusion was reached when there was no change with respect to time in the outlet gaseous compositions. Preliminary tests with a mass spectrometer (MiniLab) confirmed that steady state conditions were established in less than 2 minutes for all the runs. An estimation of the time to reach steady state was also obtained by using one-dimensional, time dependent diffusion model for the flux through the porous sample.

Drying columns (4214MS, Omnifit) were connected upstream to make sure that the gases were dry. They contained a general purpose 4A Molecular sieve with a moisture indicator changing from blue to white when exhausted. The system was also purged by nitrogen for 2 hours before the beginning of a new analysis to remove any impurities left in the tubing by previous runs.
4. Parameters of the Experimental Design

The experimental design for the determination of the effective diffusivities by the steady state diffusion cell method required a number of assumptions and approximations to be made. It was therefore very important to ensure that under the chosen experimental conditions, these assumptions were appropriate and valid for the current method.

In this section a brief outline of the stages involved in the experimental design is presented. The reader is referred to a more detailed study [14] in which the validity of the hypotheses made was verified by certain numerical calculations for the desired operating conditions.

4.1 Effect of Pressure Drop

The main source of error in this method was the uncontrolled pressure difference between the two sides of the porous sample in the diffusion experiments. This total pressure difference may give an unwanted convective flow contribution to the diffusion flux. Although this technique required zero pressure difference, in practice the cell was operated under small pressure drops. It was therefore necessary to become aware of the sensitivity of that small pressure drop to the changing physical properties of the gas mixture.

Poiseuille equation for laminar flow in a cylindrical tube was applied to predict the pressure driven flux through the porous ceramic sample for a typical binary gas mixture such as that of hydrogen and nitrogen. Estimates showed that convective flux through the porous sample induced by a pressure difference of 12 Pa is at least two orders of magnitude smaller than the diffusive flux. The convective contribution to the diffusive flux was less than 1% and therefore could be ignored. Calculations for both ceramic supports showed the same difference between the fluxes, with the convective flux being two orders of magnitude smaller than the diffusion flux.

4.2 Time to Establish Steady State Diffusion

Another requirement of this method was that the steady state diffusion was reached. The effective diffusivities were calculated by equations that treated the experimental diffusion data under steady state conditions. The time required for the steady state conditions to be established was therefore estimated by using a simple, one-dimensional, transient diffusion model which was that of the semi-infinite stationary medium with a prescribed mass concentration. This case is very common because any diffusion problem will behave as if the medium is infinitely thick at short enough times.

For a typical binary gas mixture used in the diffusion experiments, the predicted time to reach steady state diffusion was found to be very short (even shorter than the time found experimentally). In practice, a time of twenty minutes was allowed for the system to reach steady state before measurements were made.

4.3 The Effect of the Concentration Boundary Layer

The boundary layer was another factor that could affect the way in which the raw data were interpreted. The validity of the one-dimensional approximation for diffusion through the porous sample, and the assumption that the surface concentration on each side of the porous sample was equal to the bulk concentration of the gas on the bulk stream of the fluid, were all closely related to the boundary layer issue.

Calculations were first performed to characterise the bulk flow above the porous sample and then to estimate the mass transfer coefficient. For given operating conditions the internal flow was found to be laminar. A comparison of the transport coefficients, namely the mass transfer coefficient and the effective binary diffusion coefficient, suggested that the dominant transport mechanism was the diffusion through the porous sample rather than the convection
to the surface across the boundary layer. These findings were related to the concentration differences. The comparative analysis of the transport coefficients indicated that the difference between the bulk stream concentration and the surface concentration was small. It is the concentration drop across the porous support, which is significant. This suggested that the bulk stream fluid concentration may be regarded to be approximately equal to the surface concentration.

The theoretical analysis explained also the effect of the flow rate on the mass transfer coefficient. It was shown that for laminar flow and fully developed conditions, the estimation of the convection mass transfer coefficient from the Sherwood number, is a constant, independent of parameters like the Reynolds number or the axial location. Since the Reynolds number does not influence the Sherwood number thus the feeding flow rate does not have any effect on the convection mass transfer coefficient too. Within the chosen range of flow rates from 50-100 cm³/min the flow is in the laminar regime. Therefore the independence of the convection coefficient on the flow rate holds for the whole range of the selected feed flow rates.

According to the aforementioned discussion the one-dimensional approximation made is valid because the experimental conditions are controlled so that the concentration difference across the boundary layer remains small and the diffusive flux across the porous support small but measurable.

5. Results and Discussion

5.1 Mercury Porosimetry Results

One of the most important characteristics of a porous structure is the pore volume distribution, which is the distribution of void volume according to the size of the pore. It is a very difficult problem to evaluate and/or calculate this distribution because the void spaces in a given particle are usually nonuniform in size, shape and length and normally are interconnected. These void spaces are usually simulated as cylindrical pores, and thus the size of the void spaces is interpreted as a radius of a cylindrical pore. Therefore the distribution of the pore volume is defined in terms of this variable [19]. In Figure 2, the pore volume distribution curve is shown for the CSZ sample as generated by the data obtained by mercury porosimetry.
Figure 2: Pore volume distribution of the CSZ sample. The red line corresponds to the intrusion and the blue one to the extrusion.

The pore volume distribution is prepared from the mercury penetration curve, shown in Figure 3. First the mercury porosimetry data, consisting of the values of the raw volume of the intruded/extruded mercury and the corresponding pressures, are normalised by dividing the mercury volume by the sample weight (corrected to a basis of 1 g). Then from Washburn’s equation [20],

\[ P = \frac{-2\gamma \cos \theta}{r} \]  

(8)

(where \( P \) is the applied pressure, \( \gamma \) is the surface tension of mercury, \( \theta \) is the contact angle between the mercury and the pore wall and \( r \) is the intrusion radius of the pore (assuming cylindrical pores) and the pressure, the radius corresponding to each penetration value can be calculated. The derivative of the penetration curve with respect to radius \( r \), \( dV/dr \), is the volume of pores between \( r \) and \( r + dr \) divided by \( dr \); that is the pore volume distribution function, \( D_v(r) = dV/dr \) according to pore radius. Here in this graph the distribution function is given as a function of the pore diameter and this is found by dividing the \( D_v(r) \) by 2. It is also customary to plot the pore radius or diameter in a logarithmic coordinate as shown above.)
It can be seen from Figure 2 that the distribution is reasonably symmetrical, not bidisperse, with most of the volume to lie in a pore size range from 0.7 to 3.0 µm and with a most probable pore diameter of about 2.0-2.1 µm. No pore volume was observed below 0.5 µm.

Figure 3: Porogram of the intruded and the extruded volume of mercury against pressure for the CSZ substrate. The red line corresponds to the intrusion curve and the blue one to the extrusion curve.

It is not easy to say whether the shape of the graph of intruded and extruded curves, shown in Figure 3, is a clear indication of a sample with controlled, open-ended pores. However, it is shown from the rather symmetrical shape of the pore volume distribution curve, in Figure 2, that the CSZ sample consists of pores of uniform diameter rather than possessing a wide range of pore sizes. It is evident from the intrusion curve that the majority of the pores are concentrated around the pore diameter of 2.0 µm which appears to be the most probable pore diameter.
The pore volume distribution curve for the MMA substrate is presented in Figure 4:

![Figure 4: Volume pore size distribution of the MMA sample. Intrusion is indicated by the red curve while the blue one shows extrusion.](image)

The distribution curve is quite symmetrical with most of the pore volume to be found in a pore diameter range from 0.5 to 3.0 \( \mu m \) with a most probable pore diameter of about 2.1 to 2.2\( \mu m \). The shape of the distribution curve of the MMA appears to be very similar to the corresponding plot of the CSZ sample. The pore sizes are equally similar, with that one of the CSZ to extend down to 0.7\( \mu m \).

### 5.2 Physical Properties of Porous Substrates

Table 1, contains all the geometrical properties measured by mercury porosimetry for the two substrates.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean volume (m³/kg) x10⁵</th>
<th>Total intruded volume (m³/kg) x10⁵</th>
<th>Mean surface area (m²/kg)</th>
<th>Total surface area (m²/kg)</th>
<th>Bulk density (apparent) (kg/m³) x10³</th>
<th>True (skeletal) density (kg/m³) x10³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSZ</td>
<td>3.92 at a diameter of 1.8 µm</td>
<td>5.82</td>
<td>71 at a diameter of 1.8 µm</td>
<td>127</td>
<td>3.74</td>
<td>4.78</td>
</tr>
<tr>
<td>MMA</td>
<td>4.98 at a diameter of 1.3 µm</td>
<td>5.75</td>
<td>95 at a diameter of 1.3 µm</td>
<td>176</td>
<td>2.75</td>
<td>3.27</td>
</tr>
</tbody>
</table>

Table 1: Structural properties of the porous substrates taken from the intrusion statistics.

It is observed that the CSZ sample has slightly greater total intruded volume than the MMA which presents bigger mean and total surface area per sample kilogram. The CSZ also has higher bulk and true density.

The bulk density is defined as the solid mass divided by the volume occupied by the solid, including pores and any interparticle voids. It is also known as apparent density and is less than the true density. The latter is defined as the ratio of the mass of the solid to the volume occupied by that mass excluding contributions from pores or internal voids. It is also called the skeletal density.

A series of additional results can be generated using the basic structure properties taken from the mercury porosimetry results:

a) Given the total intruded pore volume per gram and the sample weight, the pore volume can be calculated:

\[
pore\ \text{volume} = \left( \frac{\text{total intruded pore volume per kg}}{\text{sample weight}} \right) = \left( 5.82 \times 10^{-5}\ \text{m}^3\text{kg}^{-1} \right) \left( 74.58 \times 10^{-5}\ \text{kg} \right) = 4.34 \times 10^{-8}\ \text{m}^3
\]  

This value for the pore volume agrees with the total intruded volume shown by the penetration curve in Figure 3, as the maximum point of the curve corresponds to a raw volume value of about 0.043 cm³ or \(4.30 \times 10^{-8}\ m³\).

b) The void fraction or open porosity of the porous sample is obtained by applying the following equation:

\[
\varepsilon_p = \frac{\text{pore volume}}{\text{total bulk sample volume}} = \frac{4.34 \times 10^{-8}\ m³}{19.94 \times 10^{-8}\ m³} = 21.77\%
\]  

When the bulk and true density of the material are known, an alternative expression for calculating the open porosity is the following:

\[
\varepsilon_p = 1 - \frac{\rho_{\text{bulk}}}{\rho_{\text{true}}}
\]
c) The solids fraction is given by the following equation:

\[
\varepsilon_p + \varepsilon_s = 100\% \\
\varepsilon_s = 100 - 21.77 = 78.23\%
\]

\[ (12) \]

d) The bulk density is easily determined by:

\[
\rho_{\text{bulk}} = \frac{(\text{sample weight})}{(\text{sample bulk volume})} = \frac{74.58 \times 10^{-5} \text{kg}}{19.94 \times 10^{-8} \text{m}^3} = 3.74 \times 10^3 \text{kg/m}^3
\]

\[ (13) \]

The value of the bulk density is in exact agreement with that estimated by the mercury porosimetry.

e) Finally, the density of the solid phase (true density) can be calculated according to the expression:

\[
\rho_{\text{true}} = \frac{(\text{sample weight})}{(\text{bulk volume} - \text{pore volume})} = \frac{74.58 \times 10^{-5} \text{kg}}{(19.94 - 4.34) \times 10^{-8} \text{m}^3} = 4.78 \times 10^3 \text{kg/m}^3
\]

\[ (14) \]

The calculated value agrees exactly with the value of the true density in Table 1, as measured by the mercury porosimetry method. Performing similar calculations the corresponding properties of the MMA sample may be determined. All the values for the two samples are shown in Table 2,

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample weight (kg)x10^-5</th>
<th>Bulk sample volume (m³)x10^-8</th>
<th>Pore volume (m³)x10^-8</th>
<th>Porosity</th>
<th>Solids fraction</th>
<th>Bulk density (kg/m³)x10^3</th>
<th>True density (kg/m³)x10^3</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSZ</td>
<td>74.58</td>
<td>19.94</td>
<td>4.34</td>
<td>21.77%</td>
<td>78.23%</td>
<td>3.74</td>
<td>4.78</td>
</tr>
<tr>
<td>MMA</td>
<td>89.13</td>
<td>32.40</td>
<td>5.13</td>
<td>15.83%</td>
<td>84.17%</td>
<td>2.75</td>
<td>3.27</td>
</tr>
</tbody>
</table>

Table 2: Structural properties of the porous substrates calculated using data generated by mercury porosimetry.

From the two porous substrates the CSZ has higher porosity than the MMA. Interestingly the values of bulk and true density calculated are in precise agreement with those ones measured by mercury porosimetry.
5.3 Effective Diffusivities

Two pairs of gases, consisting of N\textsubscript{2} with H\textsubscript{2} and CO were used for the measurement of the diffusion coefficients through the CSZ and MMA porous substrates. The diffusion experiments were analysed under conditions of one-dimensional diffusion in a isothermal, inert, binary gas mixture through a porous medium with zero pressure difference across it.

To calculate the effective binary diffusivities, the diffusive flux through the porous support along with the concentrations of the gases at the two faces of the porous support are required. The compositions of the inlet and outlet gas streams were obtained by gas chromatography analyses, while the experiments were carried by feeding known inlet flow rates of the gases. The processing of the raw data involved, first, comparison with the results from the calibration analysis and then normalisation to give 100%. Finally the diffusion fluxes of each gas in porous support were determined from mass balances on each stream.

The values of the effective diffusion coefficients for the gas mixture of H\textsubscript{2}-N\textsubscript{2} are summarised in Tables 3 and 4:

<table>
<thead>
<tr>
<th>CSZ support</th>
<th>MMA support</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2} composition (volume %)</td>
<td>D\textsubscript{eff} / H\textsubscript{2}-N\textsubscript{2} (m\textsuperscript{2}/sec) x 10\textsuperscript{-6}</td>
</tr>
<tr>
<td>5</td>
<td>4.83</td>
</tr>
<tr>
<td>10</td>
<td>5.30</td>
</tr>
<tr>
<td>20</td>
<td>5.65</td>
</tr>
<tr>
<td>Average value of D\textsubscript{eff}</td>
<td>5.26</td>
</tr>
</tbody>
</table>

Table 3: Effective diffusion coefficient of H\textsubscript{2} in N\textsubscript{2} through CSZ (at T=298K, P=1atm).

Table 4: Effective diffusion coefficient of H\textsubscript{2} in N\textsubscript{2} through MMA (at T=298K, P=1atm).

To investigate the effect of mixture composition on the effective diffusion coefficient, the values are plotted against the mole fraction of the desired gas in the binary mixture. In Figure 5.16, the effective diffusivities of hydrogen in nitrogen are plotted against the hydrogen concentration in the mixture.
In Figure 5, it is shown that the effective diffusion coefficient of hydrogen in nitrogen increases with the mole fraction of hydrogen. It appears to be a small, linear increase. It is therefore evident that there is a variation of diffusivity with the mole fraction of the lighter gas, which is also predicted by theory [21], but it is difficult to confirm within the given experimental uncertainty.

The binary mixture of carbon monoxide and nitrogen presents considerable interest. Because CO and N₂ have nearly identical molecular mass and the same molecular shape, size and electronic configuration they are isosteric molecules. In other words, this can be regarded to resemble the case of an isotopic mixture. This is another extreme case in which all the types of the molecular force laws are identical and the molecular masses of the components are approximately equal. In this case the binary diffusion coefficient reduces to the self-diffusion coefficient. It is more appropriate to consider this coefficient as a limiting case of the binary diffusivity. There is also no composition dependence and the self-diffusivity [D]₁ is only a function of the reduced temperature. The expression [21,22] for the self-diffusivity is described by Equation (15):

\[
D = 0.0018583 \sqrt{\frac{T^3}{M}} \frac{1}{p\sigma^2\Omega_D} 
\]

where \( D \) is the self diffusivity in \( cm^2/s \), \( T \) is the absolute temperature in Kelvin, \( p \) is the pressure in atm, and \( M \) is the molecular weight, the same for both molecules. The dimensionless quantity \( \Omega_D \) is the diffusion collision integral. It is a function of the dimensionless temperature \( kT/\varepsilon_{dd} \) and depends on the choice of intermolecular-force law between colliding molecules. The parameter \( \varepsilon_{dd} \) is the characteristic energy, and \( \sigma \) is the characteristic diameter of the molecules, often called the collision diameter, and it is given in Å. This quantity also depends on the intermolecular-force law selected. According to the kinetic theory of gases no composition dependence is predicted for the self-diffusivity.
No obvious effect of the mixture composition on the measured diffusion coefficients is evident from the plots, in Figure 6. Therefore the prediction from the theory is consistent with the measured values of the binary diffusivity.

6. Conclusions
The method discussed has been successful in obtaining experimental diffusion data through two porous samples for two binary gaseous mixtures.

The effective diffusivities for a number of binary gaseous mixtures have been obtained by using the steady state diffusion cell technique. The composition dependence of the effective diffusion coefficients has been examined. No effect of the concentration of the gas under analysis was found within the accepted experimental uncertainty. In general the measured diffusion coefficients of the gases through the CSZ support are greater than those in the MMA support.
References


