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ABSTRACT

The objective of this paper is to present an engineering model based on fundamentally sound but simplified treatment of mass diffusion phenomena for practical predictions of the effective diffusion coefficient of gases through closed-cell foams. A special attention was paid to stating all assumptions and simplifications that define the range of applicability of the proposed model. The model developed is based on the electrical circuit analogy, and on the first principles. The analysis suggests that the effective diffusion coefficient through the foam can be expressed as a product of the geometric factor and the gas diffusion coefficient through the foam membrane. Validation against experimental data available in the literature gives satisfactory results. Discrepancies between the model predictions and experimental data have been observed for gases with high solubility in the condensed phase for which Henry's law does not apply. Finally, further experimental data concerning both the foam morphology and the diffusion coefficient in the membrane are needed to fully validate the model.

Keywords: gas diffusion, aging, effective diffusion coefficient, closed-cell foam.

NOMENCLATURE

b	Wall thickness in the cubic model
C	Mass concentration
d	Cell wall thickness
D	Diffusion coefficient
E	Activation energy, Equation (7)
f	Fugacity

G	Geometric factor, Equation (26)
H_f	Thickness of the foam layer
$\vec{i}, \vec{j}, \vec{k}$	Unit vectors in the x-, y-, and z-directions, respectively
j_m	Mass transfer rate
$< l >$	Average distance between successive membranes in the foam, Equation (3)
L	Linear dimension of the unit cubic cell
M	Molecular weight of the gas
n	Average number of cells across the foam layer in the direction of the diffusion process ($= H_f/L$)
p	Pressure of the gas in the void
Pe	Permeability coefficient
R_m	Species diffusion resistance
R	Universal gas constant = $8.314 J/mol.K$
S	Solubility of the gas species in the condensed phase
T	Temperature
z	Axial coordinate

Greek symbols

β	Dimensionless wall thickness in the cubic model (=b/L)
ϵ	Parameter, Equation (3)
Γ	Foam porosity function, Equation (27)
ϕ	Porosity
φ	Function of number of closed-cells in the diffusion direction, Equation (27)

Subscripts

0	Refers to a reference state
c	Refers to condensed phase (liquid or solid)
eff	Refers to effective property
f	Refers to foam
g	Refers to gas phase
i	Index of the gas species
STP	Standard temperature and pressure

INTRODUCTION

Closed-cell foams consists of gas bubbles separated one from another by a thin membrane of a continuous condensed phase. The condensed phase can be solid or liquid. Among foams having solid membrane, the polymeric foams are the most commonly used [1]. They can be rigid or flexible and the cell geometry can be open or closed. Open-cell polymeric foams are generally flexible and best for automobile seats, furniture, and acoustic insulation. Closed-cell polymeric foams are usually rigid and mostly used for thermal insulation in the construction and refrigeration industries. Indeed, closed-cell foams are very effective thermal insulators due to entrapped blowing agents used for foaming and having a low thermal conductivity. Unfortunately, the thermal insulating properties and dimensional stability of rigid closed-cell foams decay significantly with age due to the outward diffusion of the low conductivity blowing agent and the inward diffusion of higher conductivity air constituents [2, 3]. Typically, air constituents diffuse through foam much faster than commonly used blowing agents such as chlorofluorocarbons [1, 2]. As a result, the short and intermediate term aging of polymeric foams are due to in-diffusion of air constituents, while long-term aging depends on depletion of blowing agents.

Liquid foams are frequently encountered as a by-product in bioprocessing (protein separation) and materials processing (glass melting and casting) or generated for special applications (firefighing). For example, in glass manufacturing liquid foams are formed at the free surface of the molten glass due to entrapment of gas bubbles produced as a result of the batch fusion and fining reactions in the glass melt [4, 5]. Glass foams consist of spherical and/or polyhedral gas bubbles surrounded by liquid lamellae. In the glass melting process, foaming is undesirable since it reduces significantly heat transfer rates from the combustion space to the melt [4, 5], thereby increasing the operating temperature, the NO_x-formation rate, and the energy consumption [4].

Understanding and modeling of the mass diffusion process in foams is, therefore, of major importance from both fundamental and practical viewpoints. The objective of this paper is to present an engineering model based on fundamentally sound but simplified treatment of mass diffusion phenomena for practical predictions of the effective diffusion coefficient of gases through a foam layer. The model developed is based on the electrical circuit analogy, and available experimental data are used for model validation.

ANALYSIS

Current state of knowledge

In general, the effective diffusion coefficient of a gas species "i" in the foam depends not only on the diffusion coefficients in the gas and the condensed phases (denoted $D_{g,i}$ and $D_{c,i}$, respectively) but also on the foam morphology parameters such as the membrane (or wall) thickness, the unit cell size and shape, the spatial distribution of the cells, the total number of open cells and on the foam porosity [2, 3, 6, 7]. The foam porosity ϕ is defined as

$$\phi = \frac{\rho_c - \rho_f}{\rho_c - \rho_g} \tag{1}$$

and it can be easily computed from the experimental measurements of the foam density (ρ_f) and the gas and condensed phases densities, denoted by ρ_g and ρ_c, respectively. The geometry of the unit cell may vary substantially within the same foam, but an idealized unit cell of high porosity foams can be represented by a regular pentagonal dodecahedron [1, 8]. The presence of open cells tends to increase the effective diffusion coefficient and in polymeric foams, open cells account for 5% to 15% of the total number of cells [7].

The prediction of gas diffusion through the closed-cell foam can be accomplished via two different types of models [7]: 1) permeability models and 2) diffusion models. Both models use either continuous or discrete approaches. Brandreth [7] reviewed advantages and drawbacks of each model. In brief, the permeability models are based on the assumption that the permeability coefficient for species "i" through the membrane ($Pe_{c,i}$) can be expressed as the product of the diffusion coefficient ($D_{c,i}$) and the solubility ($S_{c,i}$) of the species "i" in the membrane, i.e.,

$$Pe_{c,i} = D_{c,i} S_{c,i} \tag{2}$$

This relationship is strictly valid only if steady state conditions are attained, the wall material is mainly amorphous, and the Henry's law is applicable. Brandreth [7] questioned the appropriateness of Equation (2) in studying the aging of polymeric foams by virtue of the fact that the steady state and the Henry's law conditions are hardly satisfied in practice. Ostrogorsky and Glicksman [3, 6] developed a discrete permeability model based on the electrical circuit anology and Equation (2) resulting in the following expression for the effective diffusion coefficient through the foam layer:

$$D_{eff}|_{f,i}(T) = \epsilon \frac{< l >}{d} \frac{T}{T_{STP}} Pe_{c,i} \tag{3}$$

where $< l >$ is the average distance between successive membranes, d is the membrane thickness, and $Pe_{c,i}$ is the permeability coefficient of the gas through the membrane that follows an Arrhenius type of law [6]. The parameter ϵ is defined as the ratio of the membrane area to the cross-section area of a unique cell, and it is assumed to be equal to 2 corresponding to spherical shape gas bubbles. The effective diffusion coefficients were found to underpredict the experimental results by as much as 29% [6], while in other studies [9] the discrepancies between predictions and measurements were in the range of 25% to 45%. Shankland [10] modified Equation (3) as follows:

$$D_{eff}|_{f,i}(T) = G p_{_{STP}} \left(\frac{T}{T_{_{STP}}} \right) Pe_{c,i} \tag{4}$$

where G is a dimensionless geometric factor depending on the foam structure. Equation (4) suggests that a plot $D_{eff}|_{f,i}(T)$ versus $p_{_{STP}} \left(\frac{T}{T_{_{STP}}} \right) Pe_{c,i}$ should be a straight line passing through the origin and whose slope is the geometric factor G [10]. Indeed, experimental data obtained for extruded polystyrene foams [10] support the mathematical form of Equation (4), but the author emphasized a need for additional information about the foam morphology to fully validate the model. However, there appears a clear lack of consistency in the experimental data presented by various authors. Specifically, Page and Glicksman [11] as well as Fan and Kokko [12] reported the experimental results obtained for different foams over the temperature range of 30^{o}C to 80^{o}C. Their experimental data indicate that the effective diffusion coefficient follows an Arrhenius type of law, thereby restricting the applicability of the model proposed by Shankland [10].

The continuous diffusion models consider the foam as a homogeneous and isotropic medium through which gas species "i" diffuses with an effective diffusion coefficient $D_{eff}|_{f,i}$. The effective diffusion coefficient is determined via an inverse solution of the following species conservation equation:

$$\frac{\partial C_i}{\partial t} = D_{eff}|_{f,i} \nabla^2 C_i \tag{5}$$

The discrete diffusion models consider the foam layer as the repetition of unit cells characterized by their geometry (membrane thickness, cell size and shape) as well as the diffusion coefficients of the species through the condensed phase (liquid or solid) and through the gas phase. Several studies showed the significant influence of the foam morphology on the diffusion process through closed-cell foams [13, 14]. The continuous model is by its essence unable to account for the discreteness of the foam morphology. In contrast, the discrete approach enables one to express the effective diffusion coefficient in terms of parameters characterizing the foam structure and composition.

Recently, Alsoy [15] reviewed the discrete diffusion models, and a reader is referred to this publication for citations of the relevant literature. In short, she concluded that the model developed by Bart and Du Cauzé de Nazelle [16] represents the current state-of-the-art. In this work, one-dimensional diffusion through a series of three-dimensional cubic cells of uniform wall thickness was considered. The authors neglected the diffusion through the gas phase, and used the Henry's law at the membrane/gas phase interface to obtain the following expression for the effective diffusion coefficient both in a unit cell and in the entire foam [16, 17]:

$$D_{eff}|_{f,i}(T) = \left(\frac{L}{b}\right)\left(\frac{D_{c,i}S_{c,i}RT}{(1-\phi)S_{c,i}RT+\phi}\right) \tag{6}$$

Here, $D_{eff}|_{f,i}(T)$ is the effective diffusion coefficient of gas "i" expressed as a function of geometric parameters of the foam [the size of the unit cubic cell (L), the thickness of the membrane (b), and porosity (ϕ)], and thermophysical properties [the diffusion coefficient ($D_{c,i}$) and the solubility ($S_{c,i}$) of the gas in the condensed phase]. Alsoy [15] reported an extensive comparison of the effective diffusion coefficient predicted by Equation (6) with the experimental data obtained for different types of polymeric foams and diffusing gases. The author observed that Bart and Du Cauzé de Nazelle's model underpredicted the effective diffusion coefficients by about one to three orders of magnitude [15].

To conclude this overview, there is a great deal of controversy about what type of model should be used for predicting the effective properties of a foam. In this paper, an attempt is made to derive an expression of the effective diffusion coefficient of the foam based on the first principles. It is hoped that the theoretical model developed will contribute to clarifying at least some of the controversial issues and will provide a framework for developing physically consistent models. In the present work, a cubic unit cell is used as representative model to predict mass diffusion through the closed-cell foams using electrical circuit analogy. A special attention was paid to stating all assumptions and simplifications that define the range of applicability of the proposed model. Finally, the analysis considers multi-gas diffusion through the foam layer with either liquid or solid condensed phase. The theoretical model developed is validated against the experimental data available in the literature.

Model Assumptions

A model for mass diffusion of the gas species “i” through a unit cell of the foam layer is developed using the following assumptions:

1. Foam cells are taken to be closed and separated by the continuous solid or liquid membranes.

2. The condensed phase of the membranes is assumed to be at rest.

3. Gas diffusion of gas species “i” through the condensed phase is considered to be a thermally activated process, i.e., the mass diffusion coefficient ($D_{c,i}$) depends on the temperature via the Arrhenius’ law [18]:

   $$D_{c,i} = D_{c,0,i} exp\left(\frac{-E_{c,i}}{RT}\right) \tag{7}$$

   where $D_{c,0,i}$ and $E_{c,i}$ are experimentally determined constants.

4. The gas mixture contained in the pores (voids) of the foam behaves as an ideal gas.

5. Mass diffusion only in the vertical z-direction is considered.

6. The diffusing gas species “i” is weakly soluble in the condensed phase (i.e., Henry’s law is applicable)[1].

7. The temperature is uniform throughout the unit cell.

8. The pressure in the void remains close to the atmospheric pressure (maximum 5 atm [19]) so that the ideal gas approximation for fugacity is valid.

9. The diffusing gas neither reacts with the condensed phase nor undergoes dissociation or association.

10. The condensed phase is continuous (i.e., poreless).

11. The foam consists of a succession of identical stacked layers of juxtaposed unit cells. Thus, the effective diffusion coefficient of gas “i” through the entire foam layer ($D_{eff}|_{f,i}$) can be expressed as:

$$D_{eff}|_{f,i} = \left(\frac{L}{H_f}\right) D_{eff,i} = \frac{1}{n} D_{eff,i} \tag{8}$$

    where $D_{eff,i}$ is the effective diffusion coefficient of gas species “i” through a unit cell, H_f is the foam thickness, and L is the characteristic length of the cubic unit cell. The ratio H_f/L (=n) represents the number of unit-cell-thick layers constituting the foam. Note that, as the number of closed-cells in the diffusion direction increases, the resistance to gas diffusion increases and the effective diffusion coefficient becomes smaller.

12. Convective gas transport inside the pores is neglected [11].

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[1] This assumption appears not to be valid for $CFCl_3$ (R-11) in rigid polyurethane foams as discussed by Brandreth [7].

13. The changes of the effective diffusion coefficient due to the variation of the foam porosity with temperature (i.e., due to thermal expansion) are neglected compared to the changes due to the variation of the diffusion coefficients $D_{c,i}$ and $D_{g,i}$ with temperature.

Using the above listed assumptions, a model for effective diffusion coefficient in closed-cell foams is developed based on the cubic representation of the foam unit cell.

Cubic Unit Cell Model

Figure 1 shows a representative unit cell that is used to describe the microstructure of the foam. The unit cell is a cube of characteristic length L with the pore (void) represented by a smaller cube. The space between the two cubes is occupied by a condensed phase (solid or liquid), while the internal cube contains a gas mixture. Based on the definition of porosity (the volume fraction of the cell occupied by the gas mixture), the relationship between the wall (membrane) thickness b and the porosity ϕ can be expressed as

$$\phi = \left(1 - 2\frac{b}{L}\right)^3 \tag{9}$$

or, in terms of the dimensionless wall thickness $\beta = b/L$, as

$$\beta = \frac{1}{2}(1 - \sqrt[3]{\phi}) \tag{10}$$

Three different resistances to diffusion of species "i" in the vertical direction from the top to the bottom of the unit cell should be considered: 1) the resistance of the condensed phase, 2) the interface resistance and 3) the resistance of the gas. Wet foams are often stabilized by the surface active chemicals present at the interface of the lamella. In this analysis, it is assumed that the resistance to the mass transport provided by the surfactants is negligibly small. It is also assumed that the magnitude of the mass flux is relatively small, so that the variations of mass concentration of gas species "i" in both phases are small as well. Then, the quasi-equilibrium conditions can be assumed to exist at the gas/condensed phase interface [20] which imply the equality of the chemical potentials of the diffusing gas on both side of the interface. This fact, combined with assumptions 6, 7, 8 and 9, allows us to apply the generalized Henry's law to obtain a relationship between species concentrations on both sides of the gas/condensed phase interface [21]:

$$C_{c,i} = S_{c,i} M_i f_{g,i} \tag{11}$$

Here, $C_{c,i}$ is the concentration and $S_{c,i}$ is the solubility of the diffusing gas "i" in the condensed phase, M_i is the molecular weight of the species "i", and $f_{g,i}$ the fugacity of the species "i" in the gas phase. Provided that the pressure is low enough and ideal gas approximation holds (assumption 8), the fugacity $f_{g,i}$ is approximately equal to the partial pressure of species "i" (p_i) on the gas side of the interface [19], so that

$$C_{c,i} = S_{c,i} M_i p_i \tag{12}$$

Using an ideal-gas equation of state (assumption 4), the concentration of the gas species "i" in the gas phase can be expressed as

$$C_{g,i} = \frac{M_i}{RT} p_i \tag{13}$$

This results in the following jump condition for the species concentrations at the interface:

$$C_{c,i} = S_{c,i} R T C_{g,i} \tag{14}$$

Figure 2 schematically illustrates the mass concentration profile of gas species "i" across the foam unit cell with the jump condition at the gas/condensed phase interfaces given by

Equation (14). Note that, although the concentration profile may appear counter-intuitive, the chemical potential profile, if plotted, would be a continuous, decreasing function from top to bottom indicating the direction of the mass transfer.

Using the electric circuit analogy [22], the equivalent diffusion resistance circuit for the given unit cell can be constructed as shown on Figure 3. Here, $R_{m1,i}$ denotes the resistance of the surrounding cubic envelope, and $R_{m2,i}$ is the total resistance of the top condensed phase + void gas + bottom condensed phase layers in the center part of the unit cell. The resistance $R_{m1,i}$ can be computed in a straight-forward fashion as

$$R_{m1,i} = \frac{L}{4D_{c,i}b(L-b)} \tag{15}$$

Considering only the center part of the cube, the concentration difference across each phase can be expressed in term of the local mass-transfer rate $j_{m2,i}$ (in kg/s) and the mass diffusion coefficient of the species "i" in the given phase:

$$\begin{aligned} j_{m2,i} &= D_{c,i}(L-2b)^2 \frac{(C_{1,i} - S_{c,i}RTC_{3,i})}{b} \\ &= D_{g,i}(L-2b)^2 \frac{(C_{3,i} - C_{4,i})}{(L-2b)} \\ &= D_{c,i}(L-2b)^2 \frac{(S_{c,i}RTC_{4,i} - C_{2,i})}{b} \end{aligned} \tag{16}$$

Solvation of Equation (16) for $C_{3,i}$ and $C_{4,i}$ yields

$$(C_{3,i} - C_{4,i}) = \frac{D_{c,i}(L-2b)}{2D_{g,i}b + S_{c,i}RTD_{c,i}(L-2b)}(C_{1,i} - C_{2,i}) \tag{17}$$

By definition, the diffusion resistance in the center part of the cubic cell is given by

$$R_{m2,i} = \frac{(C_{1,i} - C_{2,i})}{j_{m2,i}} \tag{18}$$

or, after using Equations (16) and (17), by the following expression:

$$R_{m2,i} = \frac{2b}{D_{c,i}(L-2b)^2} + \frac{S_{c,i}RT}{D_{g,i}(L-2b)} \tag{19}$$

It is clear from Equation (19) that the total diffusion resistance in the center part of the cell ($R_{m2,i}$) consists of the resistances of the two layer of the condensed phase (the first term on the right-hand side) in series with the resistance of the gas phase (the second term on the right-hand side).

If the resistances $R_{m1,i}$ and $R_{m2,i}$ are specified, the total resistance of a unit cubic cell $R_{m,i}$ is computed as follows:

$$R_{m,i} = \frac{R_{m1,i}R_{m2,i}}{R_{m1,i} + R_{m2,i}} \tag{20}$$

Finally, the effective mass diffusion coefficient of the unit cubic cell ($D_{eff,i}$) is defined as

$$D_{eff,i} = \frac{j_{m,i}}{L(C_{1,i} - C_{2,i})} = \frac{1}{R_{m,i}L} \tag{21}$$

and, by substituting Equations (15) and (19) into Equations (20) and (21), it is given by

$$D_{eff,i} = D_{c,i}\left[4\beta(1-\beta) + \frac{D_{g,i}(1-2\beta)^2}{2D_{g,i}\beta + S_{c,i}RTD_{c,i}(1-2\beta)}\right] \tag{22}$$

where the dimensionless wall thickness β can be calculated from Equation (10) if the foam porosity (ϕ) is known.

In most of the practical cases, the cell interior (void volume) does not introduce a significant resistance to mass diffusion [2, 3, 16] since diffusion coefficient in the gas phase is much larger than diffusion in the condensed phase ($D_{g,i} \gg D_{c,i}$). Then, the concentration across the gas phase can be assumed as essentially constant and Equation (22) simplifies to

$$D_{eff,i} = \frac{D_{c,i}}{2\beta}(1 - 4\beta + 12\beta^2 - 8\beta^3) \tag{23}$$

Substituting an expression for β from Equation (10) into Equation (23) yields:

$$D_{eff,i} = D_{c,i}\left(1 + \frac{\phi}{1 - \sqrt[3]{\phi}}\right) \tag{24}$$

Note that if the diffusion within the void is neglected, the total diffusion resistance of the cell consists only of that of the condensed phase, and the interfacial jump conditions and the solubility of the gas in the condensed phase have no influence on the effective diffusion coefficient.

Finally, by accounting for the temperature dependence of the mass diffusion coefficient in the condensed phase $D_{c,i}$ [see Equation (7)] and considering multiple unit-cell structure of the foam layer [see Equation (8)], the following expression for the effective diffusion coefficient of the entire foam layer can be suggested:

$$D_{eff}|_{f,i} = G(\phi, n) D_{c,0,i} exp\left(\frac{-E_{c,i}}{RT}\right) \tag{25}$$

where the geometric factor $G(\phi, n)$ is expressed as

$$G(\phi, n) = \frac{1}{n}\left(1 + \frac{\phi}{1 - \sqrt[3]{\phi}}\right) \tag{26}$$

Note that the effective diffusion coefficient of the foam [Equation (25)] is expressed as the product of a geometric factor, $G(\phi, n)$, and the diffusion coefficient in the foam condensed phase, $D_{c,i}(T)$. The geometric factor $G(\phi, n)$ depends on the foam porosity (ϕ) and on the average number of cells (n) across the foam thickness in the direction of the diffusion flux. The cubic cell geometry is, obviously, a simplified representation of the real morphology of the foam. Therefore, the parameter n (=H$_f$/L) should be viewed as the number of equivalent cubic cells that best represent the real foam. Assigning an appropriate value of the linear dimension of the unit cubic cell L could be used to account for the discrepancy between the model and the reality. For example, one can derive the characteristic length by preserving one or several foam parameters (e.g., the wall thickness, the interfacial area, the cell volume or the projected interfacial area onto a plan perpendicular to the direction of diffusion) in the actual and idealized (model) settings.

The diffusion coefficient of gas species "i" in the condensed phase depends on the physical and the chemical characteristics of the condensed phase. For example, the gas diffusion coefficient in a polymeric condensed phase depends not only on the chemical structure of the specific polymer but also on morphology, density, crystallinity and orientation of molecular chains in the polymer [18]. However, the chemical structure can be considered to be a predominant factor [18], and one should carefully consider it in validating and making practical calculations using the theoretical models developed.

RESULTS AND DISCUSSION

Parametric Calculations

First, a critical analysis of the model developed by Bart and Du Cauzé de Nazelle [16] [see Equation (6)] is presented and important trends are discussed. A main input parameter for the Bart and Du Cauzé de Nazelle's model is the product $S_{c,i}RT$, whose typical values at O^{o}C in polyurethane foams range between 0.1 and 10 for nitrogen and CFC-11, respectively [16]. Figure 4 shows the ratio of the effective diffusion coefficient through a unit cell and that through the condensed phase alone, predicted by Equations (24) and (6) [for different values of the parameter $S_{c,i}RT$] ploted against the porosity (ϕ). Intuitively, one expects that as the membrane becomes thinner, the diffusion resistance decreases leading to a larger effective diffusion coefficient. In other words, the effective diffusion coefficient should increase continuously as the porosity increases since the resistance of the gas phase is much smaller than that of the condensed phase, and experimental observations confirm these expectations for low pressures [2, 11, 23]. However, when $S_{c,i}RT \leq 1.0$ (that is for nitrogen and oxygen in polyurethane membrane [16]), Equation (6) exhibits an unexpected non-monotonic trend with the local minima. This trend has also been observed by Briscoe and Savvas [24] in their numerical study of oxygen and nitrogen gas diffusion through dense polyethylene foams having an initial pressure in cavities of 4.8 MPa. The authors speculate that the medium size voids act as "buffers" which prevent rapid variation of the gas pressure in the medium porosity range, thereby leading to a local minima in the effective diffusion coefficient. In low porosity foams, the cells are too small to significantly buffer the pressure fluctuations, whereas in high porosity foams the cavities are much larger than the cell walls and their effect on pressure is negligible compared to that of the walls. For such high pressure applications, the ideal gas approximation is not valid [19] and this case falls beyond the scope of this study.

The simplified cubic model [see Equation (22)] developed here predicts a continuous increase in the effective diffusion coefficient as the foam porosity increases. The parametric analysis of the cubic model indicates that if the diffusion coefficient through the membrane is at least two orders of magnitude greater than the diffusion coefficient through the gas, then the resistance to gas diffusion presented by the gas phase can be neglected. Thus, for all practical applications with either liquid or solid condensed phase, one can neglect the resistance of the gas phase and the simplified models given by Equations (25) and (26) should be adequate for practical calculations.

Validation Against Experimental Data

Tables 1 and 2 summarize the experimental conditions used in the studies concerned with the effective diffusion coefficients through different polyurethane (PUR) and related polyisocyanurate (PIR) foams as well as other polymeric foams, respectively. Polyurethane foams and related polyisocyanurate foams comprise the largest family of rigid closed-cell foams [1]. Polyurethane membranes are formed by exothermic chemical reactions between an polyisocyanate and a polyol, and foaming is achieved by evaporation of low boiling point liquids (blowing agents) such as chlorofluorocarbons (CFC or R) (see Ref.[1] for an in depth discussion)". Note that the specific type of polyols used for polyurethane foams is rarely mentioned and often unknown to the authors [17]. This is unfortunate since previous studies [25] showed that the gas diffusion coefficient through polyurethane membranes depends on the type of polyol used, whereas the influence of the isocyanate functionality has not been clearly observed. Since $D_{c,i}$ and $S_{c,i}$ may vary by several orders of magnitude from one polyurethane foam to another [25], any reliable assessment of gas diffusion models through polyurethane foams should be performed for polyurethane foams made out of the same polyol. For instance, Alsoy [15] used the experimental data for the diffusion coefficient of an unknown type of polyurethane membrane [16] to validate the Bart and Du Cauzé de Nazelle's model against the experimental data taken from other studies without checking if the polyurethane foams were generated using the same polyol.

To assess the validity of Equations (25) and (26) for predicting the effective gas diffusion coefficient through the closed-cell foams, one needs to know (*i*) the chemical structure of the condensed phase (membrane), (*ii*) the mass diffusion coefficient of the gas through the specific membrane and its temperature dependence $[D_{c,i}(T)]$, (*iii*) the foam porosity or the foam density, and (*iv*) the average number of equivalent cubic cells in the direction of the diffusion process. Unfortunately, the authors were unable to find a consistent set of data supplied with all the necessary parameters. Therefore, an indirect approach will be used to validate the simplified diffusion models against available experimental data.

Temperature Dependence of the Effective Diffusion Coefficient

Temperature has been identified as having a significant influence on the effective gas diffusion coefficient through closed-cell foams [2]. In some cases the effective diffusion coefficient can change by one order of magnitude when the temperature is increased from 25^oC to 80^oC [2, 11]. Figure 5 shows the temperature dependence of the effective diffusion coefficient of carbon dioxide through an extruded low density polyethylene (LDPE) foam [13] and the diffusion coefficient of carbon dioxide through a polyehtylene membrane obtained in the literature [18]. One can observe that both lines have practically the same slopes, and this is in agreement with the trend predicted by the theoretical model developed in this study assuming that the variation of the geometric factor with temperature is negligible (i.e., no thermal expansion/construction occurs). Indeed, Equation (25) states that the slope of the $ln(D_{eff}|_{f,i})$ vs. $1/T$ plot and the slope of the $ln(D_{c,i})$ vs. $1/T$ plot should be the same. Note that for the cases when a temperature gradient exists across the foam layer in the direction of the diffusion flux, the discrete model can still be applied by approximating the temperature gradient as a step function with constant but different average temperatures for each unit cell in the foam layer.

Geometric Factor

As evident from Equations (25) and (26) that the ratio of the foam effective diffusion coefficient to the diffusion coefficient in the membrane is a geometric factor $G(\phi, n)$ depending on the foam morphology only. A plot $D_{eff}|_{f,i}(T)$ vs. $D_{c,i}(T)$ should, therefore, feature a straight line passing through the origin. Figure 6 depicts the experimental effective diffusion coefficient for carbon dioxide in the extruded low density polyethylene foam [13] against the diffusion coefficient through the membrane reported in the literature [18]. It appears that Equation (25) is capable of correctly predict of the trend over the temperature range of 25^oC to 50^oC within an error corresponding to the uncertainty in the experimental data.

Bart and Du Cauzé de Nazelle [16] reported data for the effective diffusion coefficient and the diffusion coefficient through the membrane for an unspecified polyurethane foam with diffusing gases being oxygen, nitrogen, carbon dioxide, CFC-11 and CFC-22. It is interesting to note that, in general, the geometric factor varies significantly from one gas to another within the same foam. However, the low solubility gases in polyurethane foam, namely oxygen and nitrogen, yield approximately the same geometric factors within the uncertainty of the measurements. The geometric factors obtained for the other gases are higher by one to two orders of magnitude without providing any clear trend. Earlier studies have shown that the Henry's law is not valid for CFC-11 in polyurethane foams due to its high solubility [7]. Note that for the polyurethane membrane considered, the solubilities of CO_2, CFC-11, and

CFC-22 are of the same order of magnitude [16], indicating that Henry's law may not be applicable for any of these gases in polyurethane foams.

Due to the lack of consistent and complete set of experimental data, the proposed theoretical model can be only approximately validated indirectly. Specifically, Equation (26) suggests that the geometric factor is the function of the foam porosity $\Gamma(\phi)$ divided by the equivalent number of cubic cells in the foam layer in the diffusion direction, i.e.,

$$G(\phi, n) = \frac{\Gamma(\phi)}{n} \tag{27}$$

Then, by considering two foam samples with different porosities but with the membrane made of the same polymer material, the ratio of the effective diffusion coefficients should be independent of the temperature and equals to the ratio of the geometric factors only:

$$\frac{D_{eff}|_{f_1,i}}{D_{eff}|_{f_2,i}} = \frac{G(\phi_1, n_1)}{G(\phi_2, n_2)} \tag{28}$$

Figure 7 shows the ratio of the geometric factors computed from the experimental data [13] for diffusion of CO_2 and He through two similar polystyrene foams having different porosities, 0.974 and 0.917. The effective diffusion coefficients through the two samples are quite different as well as the porosities, but one can note that the geometric factor appears to be practically independent of the temperature and of the nature of the gas.

The same analysis has been performed using the experimental data for two polyisocyanurate foam samples (samples 17 and 18) containing between 10 to 15 cells and made of terate-203-mutranol-9171 (T) as the polyol and the isocyanate Mondur [26]. Figure 8 shows the experimentally determined ratio of the effective diffusion coefficients through the two foams for oxygen and carbon dioxide. The same ratio has been predicted from Equation (27) by assuming, as a first approximation, that the equivalent number of cubic cells is the same as the number of cells in the real foam. Then, considering the limiting cases for which one foam has 10 cells while the other has 15 cells and vice versa, the ratio of the effective diffusion coefficients should vary between the following limits:

$$\frac{10}{15}\frac{\Gamma(\phi_1)}{\Gamma(\phi_2)} \leq \frac{D_{eff}|_{f_1,i}}{D_{eff}|_{f_2,i}} \leq \frac{15}{10}\frac{\Gamma(\phi_1)}{\Gamma(\phi_2)} \tag{29}$$

where the values for the porosity function $\Gamma(\phi)$ are 154.9 and 134.9 for samples 17 and 18, respectively. As noted on Figure 8), inequality (29) predicts the correct range for the ratio of the effective diffusion coefficients for two different gases in foam samples made of the same condensed phase. These results, using the reported number of cells across the foam layer as the equivalent number of cubic cells n, tend to confirm the theoretical model developed. Unfortunately, experimental data providing the precise number of closed-cells across the foam layer are not available.

CONCLUSIONS

This paper deals with an analysis of the gas diffusion process through closed-cell foams. A theoretical model has been developed for predicting the effective diffusion coefficient of the weakly soluble, low pressure gases through solid and wet foams based on the first principles. The analysis suggests that the effective diffusion coefficient through the foam can be expressed as a product of the geometric factor and the gas diffusion coefficient through the foam membrane. The model has been validated by comparing its predictions with available experimental data, and the following conclusions can be drawn:

- No consistent and complete set of data is available in the literature for comprehensive model validation. In particular, the reported experimental data lack information on the temperature dependence of the diffusion coefficient in the polymer membrane and on the average number of unit cell in the foam layer. This data is critically important for the development of reliable foam diffusion models.

- The available data for different types of polymeric foams support the validity of the model developed both qualitatively and quantitatively. Discrepancies between the model predictions and experimental data have been observed for gases with high solubility in the condensed phase for which Henry's law does not apply.
- Further work is needed to extend the analysis from ideal gases to real gases as well as to perform accurate and consistent model validations through carefully designed experiments.

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Figure Captions

Figure 1. *Schematic of a cubic unit cell of the foam.*

Figure 2. *Concentration profile in the center part of the cubic cell for* $S_{c,i}RT \leq 1.0$.

Figure 3. *The equivalent diffusion resistance circuit for a cubic cell.*

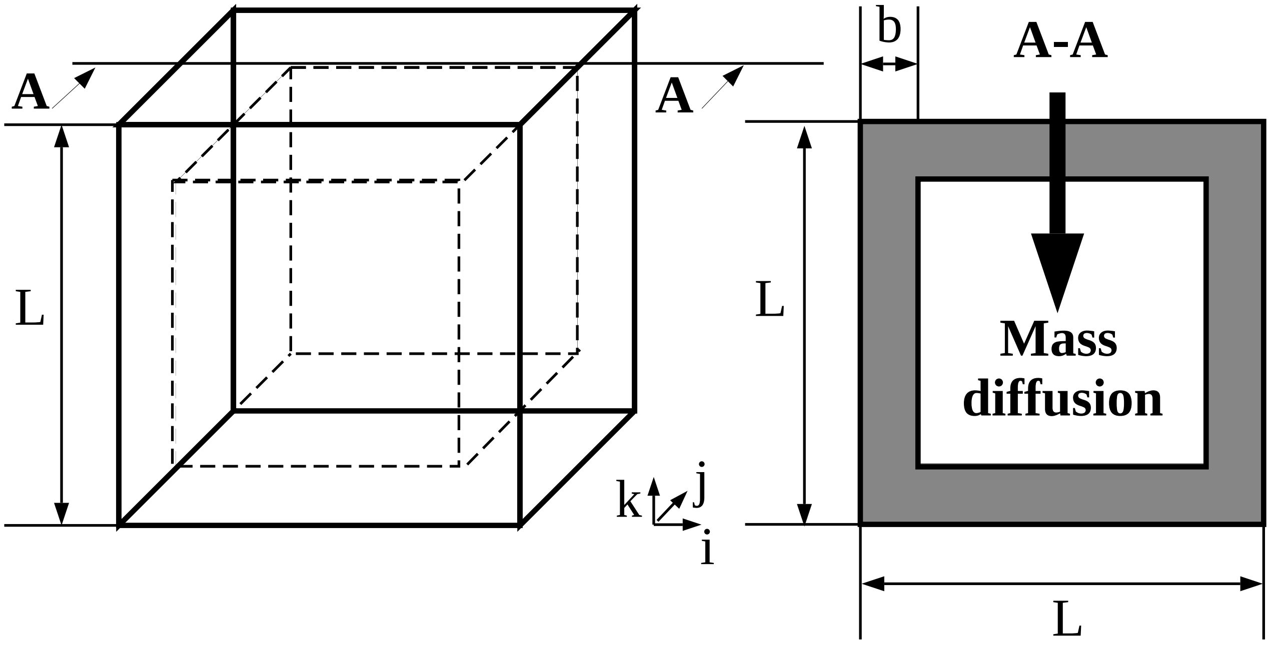
Figure 4. *Parametric analysis of Bart and Du Cauzé de Nazelle model [16].*

Figure 5. CO_2 *Diffusion coefficients through extruded LDPE foam [13] and LDPE membrane [18] vs. inverse temperature.*

Figure 6. *Effective diffusion coefficient vs. the diffusion coefficient through the membrane for* CO_2 *in extruded LDPE foam [13].*

Figure 7. *Ratio of geometric factors for polystyrene foams at different temperatures [13].*

Figure 8. *Ratio of geometric factors for PIR foams at different temperatures and predicted range [26].*



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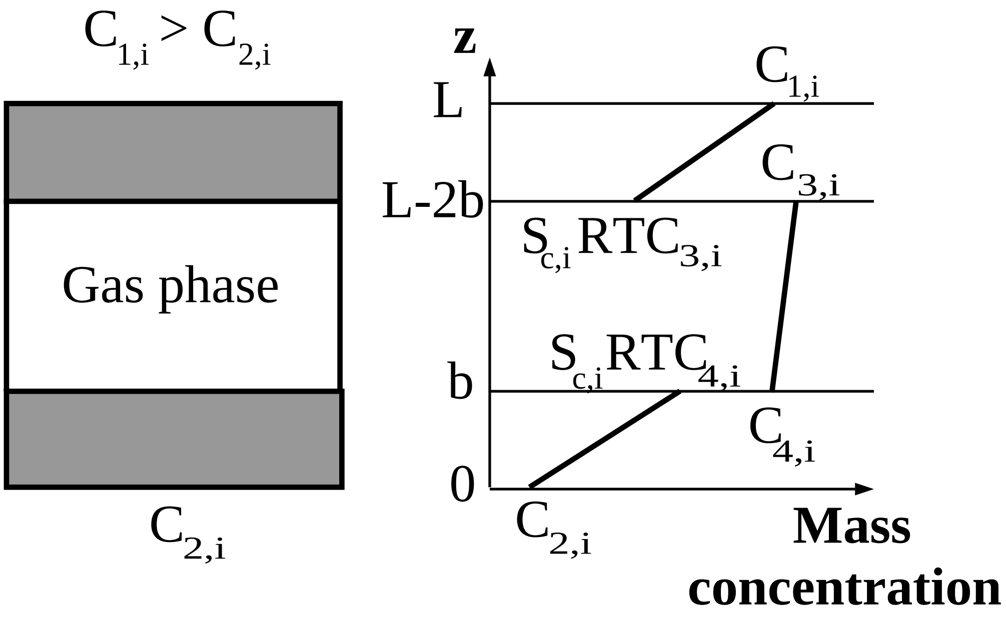

Figure 2: *Concentration profile in the center part of the cubic cell for* $S_{c,i}RT \leq 1.0$.

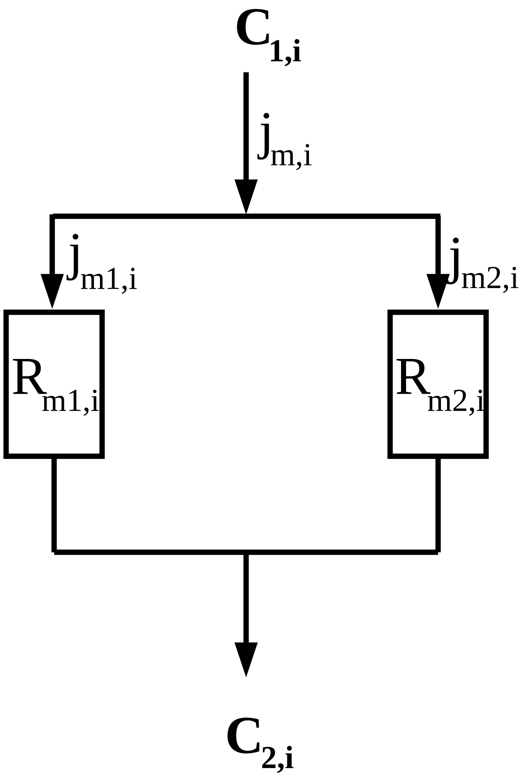

Figure 3: *The equivalent diffusion resistance circuit for a cubic cell.*

Table Captions

Table 1. *Compilation of experimental studies on gas effective diffusion coefficient through polyurethane (PUR) and related polyisocyanurate (PIR) foams.*

Table 2. *Compilation of experimental studies on gas diffusion through polymeric foams other than PUR and PIR foams.*

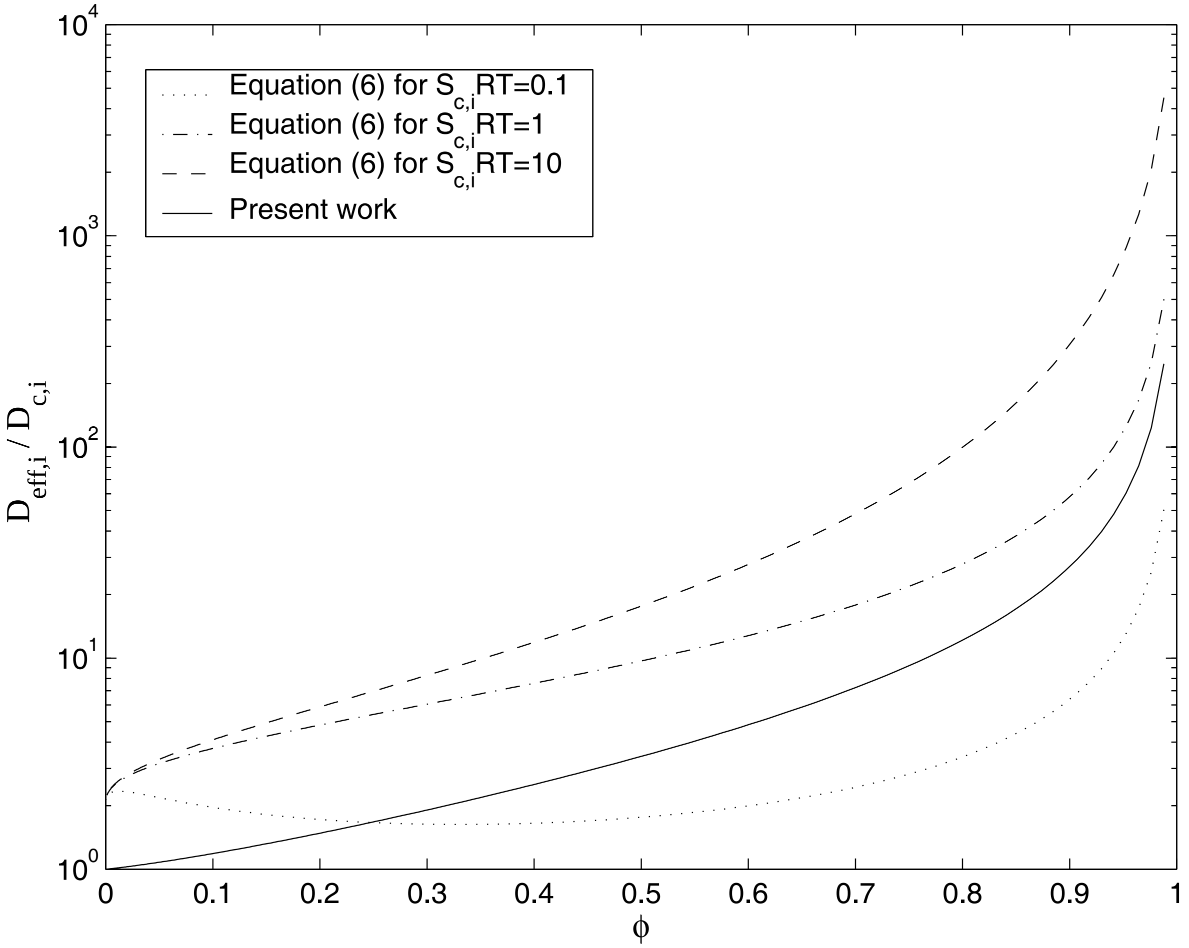

Figure 4: *Parametric analysis of Bart and Du Cauzé de Nazelle model [16].*

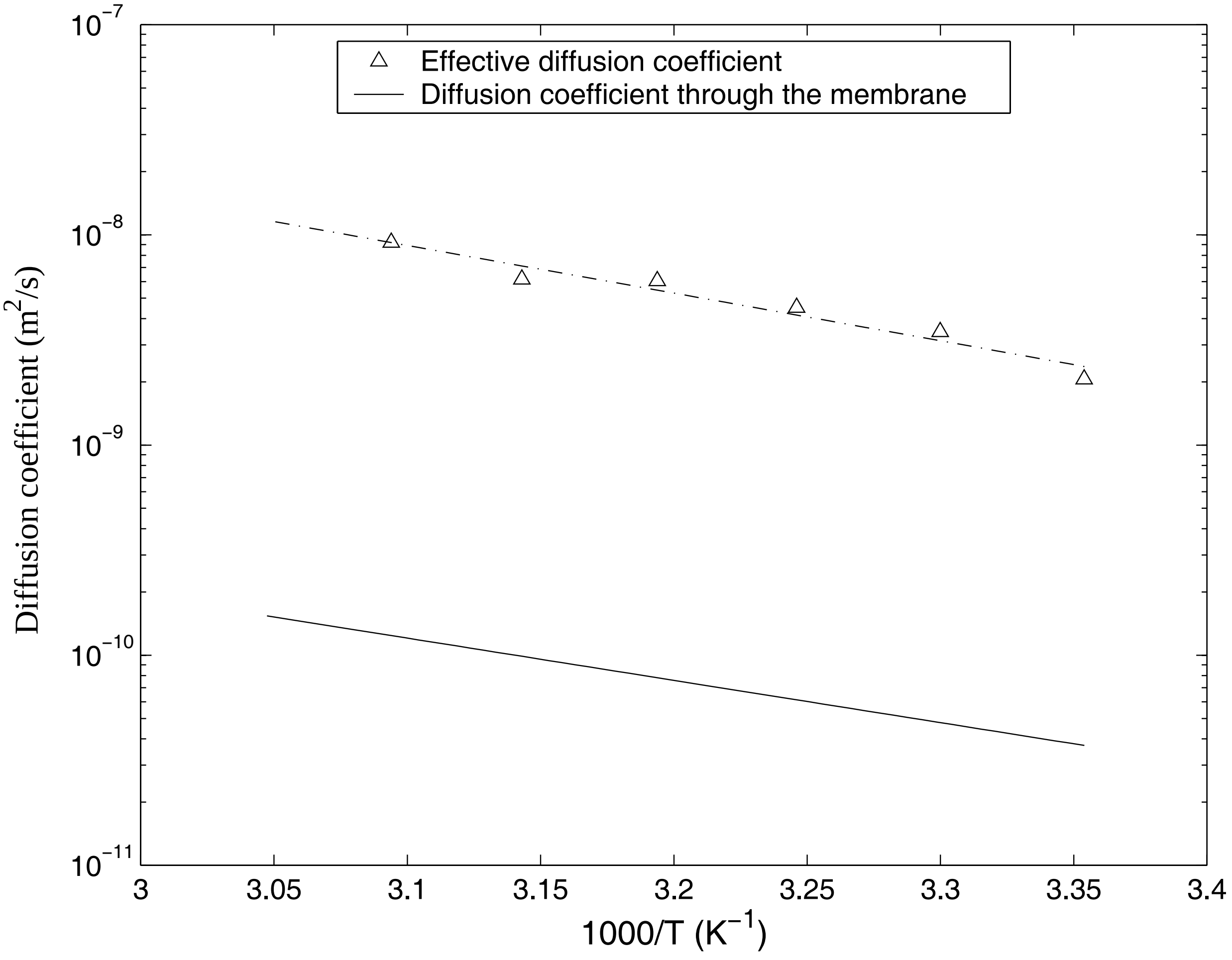

Figure 5: *CO_2 diffusion coefficients through extruded LDPE foam [13] and LDPE membrame [18] vs. inverse temperature.*

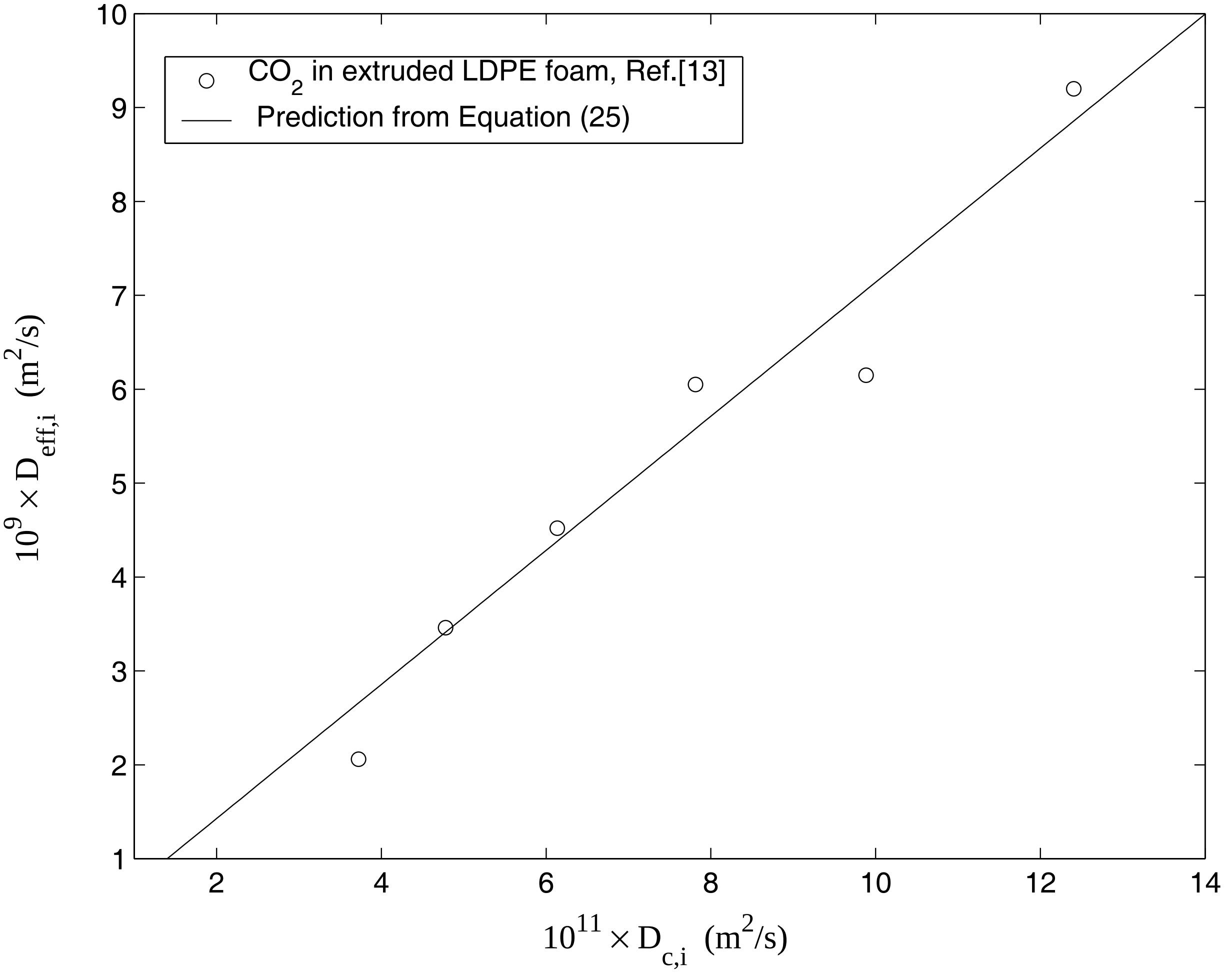

Figure 6: *Effective diffusion coefficient vs. the diffusion coefficient through the membrane for* CO_2 *in extruded LDPE foam [13].*

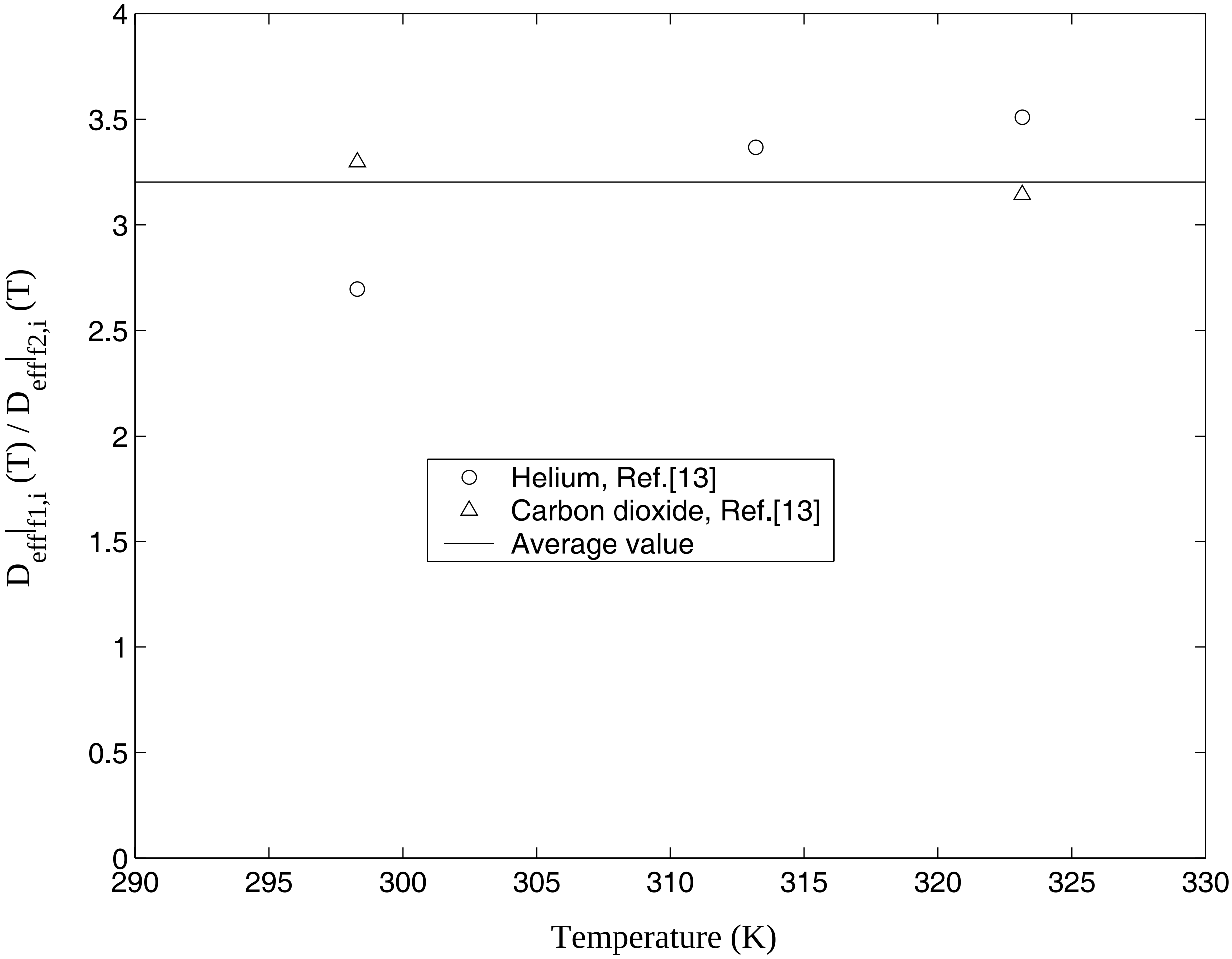

Figure 7: *Ratio of geometric factors for polystyrene foams at different temperatures [13].*

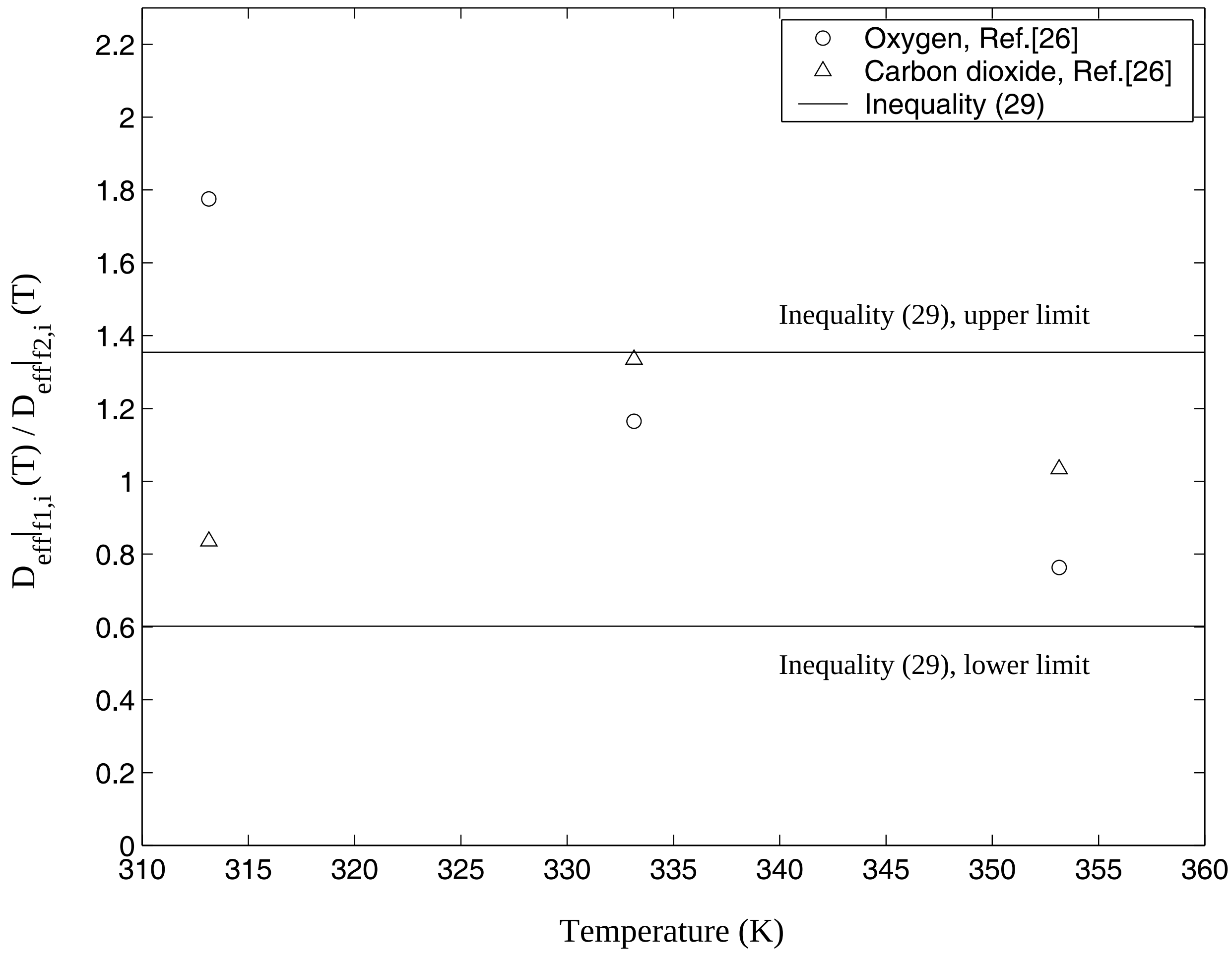

Figure 8: *Effective diffusion coefficient ratio for two PIR (MR/T) foams at different temperatures and predicted range [26].*

Table 1: *Compilation of experimental studies on gas effective diffusion coefficient through polyurethane (PUR) and related polyisocyanurate (PIR) foams.*

Ref.	**Type of Foam**	**Polyiso-cyanate**	**Polyol**	**Blowing Agent**	**Density** (kg/m^3)	**Diffusing Gases**	**Coeff.** $D_{c,i}(T)$	**Morpho-logy**
[2]	PUR	MDI	N.A.	N.A.	25.2	N_2, O_2, and R-11	N.A.	N.A.
[6]	PUR	MDI	N.A.	N.A.	22.5 to 28.4	CO_2, N_2, O_2	N.A.	A.
[9]	PUR	MDI	AP	R-11 and CO_2	30.4	CO_2	A.	A.
	PUR	MDI	ASA		34.1	air	A.	A
[11]	PIR	MR200	S-PS	HCFC-123	32.36	CO_2, O_2, N_2, R-11, and HCFC-123,-141b	N.A.	A.
	PIR	MR	T	HCFC-123	30.11		N.A.	A.
	PIR	MR	T	HCFC-141b	28.19		N.A.	A.
[12]	PUR	MDI [27]	N.A.	n-pentane iso-pentane	33 to 44.4	CO_2, N_2, and O_2	N.A.	N.A.
[13]	PUR	MDI	N.A.	R-11	27.2	CO_2, He, Ne	N.A.	N.A.
[14]	PUR	TDI	N.A.	N.A.	20.82	CO_2 and O_2	N.A.	A.
	PUR	MDI	N.A.	N.A.	28.3 to 48.1		N.A.	A.
[16]	PUR	N.A.	N.A.	N.A.	about 30 [17]	CO_2, O_2, N_2, R-11, R-22,-123,-141b	A.	N.A.
[23]	PUR	N.A.	N.A.	N.A.	31.2	N_2 and O_2	N.A.	N.A.
	PIR	N.A.	N.A.	N.A.	30.5	N_2 and O_2	N.A.	N.A.
[28]	PUR	N.A.	N.A.	cyclopentane, pentane	43 to 49	N_2, O_2, and CO_2	N.A.	N.A.
[29]	PUR	MDI	N.A.	cyclopentane, and n-pentane	N.A.	cyclopentane, n-pentane	N.A.	N.A.
	PIR	MDI	polyester		N.A.		N.A.	N.A.

MR: Mondur, MDI: diphenylmethane diisocyanate, TDI: toluene diisocyanate, S-PS: Stepan PS2852, ASA: Aromatic Sucrose Amine, AP: aromatic Polyether, T: Terate 203-Multranol 9171, N.A.: not available, A.: available.

Table 2: *Compilation of experimental studies on gas diffusion through polymeric foams other than PUR and PIR foams.*

Ref.	**Type of Foam**	**Blowing Agent**	**Density** (kg/m^3)	**Diffusing Gas**	**Diffusion Coeff.** $D_{c,i}(T)$	**Morphology**
[12]	XPS	N.A.	31.4	O_2, N_2, CO_2	N.A.	N.A.
[13]	XPS	R-12	34.8 to 87.5	He and CO_2	N.A.	N.A.
[13]	extruded LDPE	R-12 and R-114	25.2	He, CO_2, and Ne	A. [18]	N.A.
[23]	XPS	N.A.	31.4	N_2 and O_2	N.A.	N.A.
[30]	XPS	R-12 and methyl chloride	28 to 34	HCFC-22,-142b R-12 and N_2	N.A.	N.A.

N.A.: not available, A.: available, XPS: extruded polystryene, LDPE: low density polyethylene.