MASTER THESIS PROJECT

Predicting the Diffusivity of CO₂ in Substituted Amines

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Abstract

The experimental determination of the diffusivity of carbon dioxide (CO$_2$) in an amine solvent is difficult as the CO$_2$ diffuses and reacts simultaneously when absorbed into an amine solvent. As the knowledge of the diffusivity and solubility of CO$_2$ is essential to design the absorption units based on amine solvents, the nitrous oxide (N$_2$O) analogy is used in practice to estimate them. It consists of evaluating those physical properties by substituting the reacting CO$_2$ with an inert gas of a similar structure, N$_2$O. The diffusion of CO$_2$ in amine solvents is investigated using molecular dynamics (MD) simulation. Unlike experiments, MD simulation allows a direct measurement of the CO$_2$ diffusivity. In MD simulations, the reaction between CO$_2$ and the amine can be switched off. The Fick diffusion coefficients are derived from the Maxwell-Stefan diffusivities and the thermodynamic factors. Different amine solvents like monoethanolamine, diethanolamine, methyl-diethanolamine and ethylamine are investigated. The N$_2$O analogy in the monoethanolamine-water solution has been validated. We find a higher diffusivity for the monoethanolamine solvent than for the diethanolamine and methyl-diethanolamine solvent. Comparing the diffusion of CO$_2$ in the monoethanolamine and ethylamine solvents, we conclude that the presence of a hydroxyl group on the amine molecule is an obstacle to diffusion.
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Introduction

In chemical engineering, mass transfer operations refer to the unit operations that change the compositions of solutions and mixtures without involving any chemical reaction. They include, among others, the absorption, adsorption, distillation and precipitation processes. Understanding mass transfer is important for the design and optimization of the equipment used in industry. In a chemical process, mass transfer operations are necessary to purify the raw materials as well as to separate the final products from the by-products [1].

Absorption is a mass transfer operation in which molecules are taken up into the bulk of a solid or liquid substance [2]. In a carbon dioxide (CO$_2$) absorption process, the CO$_2$ leaves the gas stream to penetrate a liquid stream also called solvent. This has been widely used in industry as a way to separate CO$_2$ from other components in gas phase [3]. Nowadays, it is also a way to clean up flue gas generated by industries which produce considerable amount of CO$_2$, such as the power plants, before venting them to the atmosphere [3–6]. Since the advent of the industrial revolution, CO$_2$ emissions have grown considerably resulting in a significant increase of the CO$_2$ concentration in the atmosphere. CO$_2$ can be considered as the most important greenhouse gas produced by human activity [7, 8]. Reducing its emissions has therefore become an important scientific challenge. In this context, CO$_2$ capture techniques, such as CO$_2$ absorption, can be seen as interesting mid-term solutions.

Temperature, pressure and the nature of the solvent are some of the factors affecting the absorption [2]. By studying the mass transfer properties, it is possible to predict the suitable solvents for a particular absorption process.

Aqueous amine solutions are some of the best candidates for CO$_2$ capture as the process involved is chemisorption [9]. Two transport phenomena that take place simultaneously when the CO$_2$ is absorbed into an amine solvent are diffusion and reaction. Due to the reaction between CO$_2$ and the amine molecules, it is difficult to determine experimentally the physical properties required to design the absorption units based on amine solvents, i.e. the diffusivity and solubility. In practice, the diffusivity and solubility of CO$_2$ are evaluated by substituting the reacting CO$_2$ with an inert gas of a similar structure [10–14]. Nitrous oxide (N$_2$O) is the ideal
candidate to substitute CO$_2$ as both gases have similar molecular geometries, volumes and electronic structures [10]. This method, known as the N$_2$O analogy, can be applied using

$$ (H_{CO_2})_{amine} = (H_{N_2O})_{amine} \left( \frac{H_{CO_2}}{H_{N_2O}} \right)_{water} \quad (1) $$

$$ (D_{CO_2})_{amine} = (D_{N_2O})_{amine} \left( \frac{D_{CO_2}}{D_{N_2O}} \right)_{water} \quad (2) $$

where $H$ is the solubility and $D$ the diffusivity.

The aim of the master project is to study the diffusion of CO$_2$ in different amine solvents, investigate the effect of their structure on the CO$_2$ diffusivity and verify the N$_2$O analogy using molecular dynamics (MD) simulations. Indeed, with MD simulations, the reaction between CO$_2$ and the amine can be "switched off". This means that, unlike experiments, a direct measure of the diffusivity is possible. The design of many absorbers has been based on the N$_2$O analogy for a long time. This method can be validated from the simulation values of the CO$_2$ diffusivity in the amine solvent and the N$_2$O diffusivity in the same solvent.

The thesis is organized as follows: The first chapter explains the carbon capture process and molecular dynamics simulations used to obtain the diffusion coefficients of CO$_2$ in amine solvents. The second chapter provides the details of the different systems studied. The third chapter discusses the results of the simulations. A final conclusion is given along with a future outlook.
Chapter 1

Theory

1.1 Carbon Capture

It is important to focus on the large sources of CO₂ production to reduce significantly the emissions of CO₂ into the atmosphere. Among the different sectors, electricity generation contributes the most to the CO₂ emission [15]. The carbon capture process involves the separation of CO₂ from the effluent gas stream of the power plant and its transportation to a site where it can be sequestered [3]. The capture of CO₂ can be divided into three categories [4].

• Pre-Combustion Processes
  The removal of CO₂ prior to the combustion process requires the conversion of the fossil fuel into a form suitable for the separation of CO₂. In a coal-fired power plant, for instance, the coal undergoes the following transformations. Coal gasification allows the coal to be converted into a mixture of carbon monoxide (CO) and hydrogen (H₂) called syngas. The syngas is then shifted to CO₂ and H₂ by the water-gas shift reaction. The resulting CO₂ can be captured from the exhaust stream and H₂ is used as fuel.

• Post-Combustion Processes
  The CO₂ is captured from the flue gases produced during the combustion of the fossil fuels. The technology behind the post-combustion capture has been developed over sixty years as a way to purify flue gas streams [3].

• Oxy-Combustion Processes
  Instead of air, pure oxygen is used for the combustion of fossil fuels. The flue gas stream is therefore mainly composed of water vapor and CO₂. After removal of impurities, the water is separated by applying conditions which lead to phase separation. This results in a highly concentrated CO₂ stream. While oxy-combustion has been theoretically studied and experimentally tested, it is not yet at a commercial stage.

In the near future, the post-combustion capture process seems to be the most convenient method to achieve reduction in CO₂ emission since it only requires the
adaptation of existing plants [5]. Even if other technologies such as adsorption and membrane separation have been investigated for those systems, the current predominant technology is based on chemical absorption involving an ammonia or amine solvent. More specifically, monoethanolamine (MEA) is the most commonly used solvent [6].

The principle of the CO₂ capture process is depicted in Figure 1.1 [6]. After cleanup of particulate matter (fly ash) and pollutants such as NOₓ and SOₓ, the flue gas is introduced at the bottom of an absorption column. The flue gas flows towards the top, counter-currently to the solvent. The CO₂ is selectively absorbed into the solvent by reacting with the amine. The CO₂-rich solution is sent to a stripper column to regenerate the solvent. On heating the CO₂-rich solution, the backward reaction is favoured and the CO₂ is released. The lean solvent can be reused in the absorption column. The concentrated CO₂ gas stream is then compressed to facilitate transportation and can be stored or used for specific applications such as enhanced oil recovery [5].

Improving the design of a CO₂ capture unit and making its operating and capital costs as low as possible involve several challenges [16].

- Reduction of the heat consumption
  In the CO₂ capture process, the solvent regeneration is an energy demanding step. For example, temperatures beyond 100 °C are needed to recover MEA. Including a CO₂ capture unit lowers the efficiency of a power plant as steam is required to supply heat for the solvent regeneration.
• Advanced process flow sheet and integration
• Reduction of solvent traces emissions
• Reduction of the equipment investment

One of the main challenges of this technology is to find a solvent whose reactivity with CO$_2$ is high and, at the same time, whose energy duty for its regeneration is low [8].

In addition to a high absorption rate with CO$_2$ and a low energy requirement, there are other properties to consider while searching for an appropriate solvent. Among others, the solvent should be the least corrosive and should have a low volatility and a high selectivity. It should also not be prone to temperature and contaminant degradation. Furthermore, the economics has its importance: the lower the cost, the better [6].

1.2 Diffusion

Diffusion is the transport phenomenon that occurs due to a gradient in chemical potential in a system. The gradient of concentration can also be considered as the driving force for the diffusive mass transfer. Self-diffusion and mutual diffusion are two different notions [17]. The former characterizes the migration of individual molecules. The latter describes the collective motion of the molecules. Mass transport is thus generated by mutual diffusion. This explains why, in practice, focus is about mutual diffusion. Two approaches can be used to describe the diffusive mass transport: the Fick’s laws and the Maxwell-Stefan theory [2, 17].

Generalized Fick’s law indicates that any chemical species $i$ moves from higher to lower concentration areas [2]. It relates the molar diffusion flux of species $i$ denoted by $J_i$ to its gradient of concentration. Generalized Fick’s law for a system of $n$ components in a molar reference frame is given by

$$J_i = -c \sum_{k=1}^{n-1} D_{Fick}^{ik} \nabla x_k,$$

(1.1)

where $c$ is the total molar concentration, $D_{Fick}^{ik}$ are Fick diffusivities and $x_k$ is the mole fraction of species $k$. Since a molar reference frame is used in Eq. (1.1), the fluxes are constrained by $\sum_{i=1}^{n} J_i = 0$. For a $n$-component system, the number of Fick diffusion coefficients required for the mass transfer characterization is $(n - 1)^2$ [18].

An alternative approach to describe diffusion is the Maxwell-Stefan (MS) theory for which the gradient of the chemical potential at constant temperature and
pressure is the driving force for mass transfer [2]. This driving force is balanced by the internal friction forces between species which are proportional to their difference in average molar velocities \((u_i - u_j)\),

\[
\frac{1}{RT} \nabla_{T,P} \mu_i = \sum_{j=1, j \neq i}^{n} \frac{x_j(u_i - u_j)}{D_{ij}},
\]

(1.2)

where \(RT\) is the gas constant multiplied by the absolute temperature, \(\mu_i\) is the chemical potential of component \(i\) and \(D_{ij}\) are the MS diffusivities. The subscripts \(T\) and \(P\) indicate that the differentiation is carried out at constant temperature and pressure. The factor \(\frac{1}{D_{ij}}\) can be interpreted as a friction coefficient. The MS diffusivities are symmetric \((D_{ij} = D_{ji})\) and the number of coefficients required to fully describe the diffusion in a \(n\)-component system is \(n(n - 1)/2\). The MS diffusivities depend less strongly on the concentration than the Fick diffusivities and do not depend on a reference frame [18, 19].

Only the Fick diffusion coefficients can be obtained from experiments. In contrast, MS diffusivities can easily be obtained from MD simulations. However, since both Fick’s law and Maxwell-Stefan theory describe the same process, it is possible to relate both of them using

\[
[D] = [B]^{-1}[\Gamma],
\]

(1.3)

where matrix \([D]\) is a \((n - 1)\times(n - 1)\) matrix of Fick diffusion coefficients and \([\Gamma]\) is the so-called matrix of thermodynamic factors [20–23].

The elements of matrix \([B]\), which have no physical meaning, can be derived from the MS diffusivities [20, 23–25]:

\[
B_{ii} = \frac{x_i}{D_{ii}} + \sum_{j=1, j \neq i}^{n} \frac{x_j}{D_{ij}} \quad \text{with} \quad i = 1, \ldots, (n - 1),
\]

\[
B_{ij} = -x_i \left( \frac{1}{D_{ij}} - \frac{1}{D_{ii}} \right) \quad \text{with} \quad i, j = 1, \ldots, (n - 1).
\]

(1.4)

Matrix \([\Gamma]\) contains the thermodynamic factors. They represent the deviation from the ideality and are given by

\[
\Gamma_{ij} = \delta_{ij} + x_i \left( \frac{\partial \ln \gamma_i}{\partial x_j} \right)_{T,P,\Sigma},
\]

(1.5)

in which \(\delta_{ij}\) is the Kronecker delta and \(\gamma_i\) is the activity coefficient of component \(i\) [20, 21, 23, 24]. The symbol \(\Sigma\) indicates that the differentiation is performed at constant molar fraction except for the \(n\)th component such that the sum \(\sum_{i=1}^{n} x_i\) remains equal to 1.
1.3 Molecular Dynamics Simulation

Statistical thermodynamics provides a molecular interpretation of the behaviour of macroscopic systems. Macroscopic properties are predicted from the microscopic properties of individual atoms and molecules [26, 27]. Molecular simulation can be used as a powerful tool for statistical thermodynamics. It consists of modeling the evolution of molecular systems. From the trajectory, velocities and other properties gathered during simulation, properties of macroscopic systems can be predicted [28]. There are two main approaches in classical simulations.

In Monte Carlo (MC) simulations, the configuration of a system is updated as follows. Random positions are generated for the molecules of the system. They are accepted only under certain conditions. These conditions ensure that the probability to find the system in a particular configuration is equal to exp (−E/kT) where E refers to the energy of the considered configuration. System states with a low energy have thus a higher probability than states with a high energy. MC simulations are said to be stochastic as each system configuration depends on the previous configuration only but not on any other anterior configuration [28, 29].

In molecular dynamics (MD) simulations, the positions of the molecules in the system are updated by solving numerically the Newton’s equations of motion [28–30]. For a system of N particles, these equations can be written as

\[ m_i \frac{\partial^2 r_i}{\partial t^2} = F_i, \]

(1.6)

where \( m_i \) is the mass of particle \( i \), \( r_i \) is the position, \( F_i \) is the force acting on the particle and \( t \) the time. In contrast to the MC simulations, it is a deterministic approach: the configuration of a system at any time in the future can be predicted from its current configuration. MD simulations can be performed only for systems whose dynamics are described by classical mechanics [28].

1.4 Calculating the Diffusion Coefficients

1.4.1 Maxwell Stefan Diffusivities

It is possible to compute thermodynamic properties of a system from the trajectory of the molecules constituting the system. For instance, the self-diffusivity \( D_{i,\text{self}} \) of a component \( i \) is related to the mean square displacement of molecules of type \( i \) by

\[ D_{i,\text{self}} = \frac{1}{6N_i} \lim_{\delta t \to 0} \frac{1}{m \cdot \delta t} \left\langle \sum_{l=1}^{N_i} (r_{li}(t + m \cdot \delta t) - r_{li}(t))^2 \right\rangle, \]

(1.7)
where $N_i$ represents the number of molecules of component $i$, $\delta t$ is the time step used in the simulation, $m$ is the total number of time steps and $r_{l,i}(t)$ is the position of the $l$th molecule of component $i$ at time $t$ [28].

In a similar fashion, MS diffusivities can be found from the trajectory of molecules. They follow directly from the Onsager coefficients, $\Lambda_{ij}$, which are defined for an $n$-component system by

$$\Lambda_{ij} = \lim_{m \to \infty} \frac{1}{N} \frac{1}{m \cdot \delta t} \left( \left( \sum_{l=1}^{N_i} (r_{l,j}(t + m \cdot \delta t) - r_{l,j}(t)) \right) \cdot \left( \sum_{k=1}^{N_j} (r_{k,j}(t + m \cdot \delta t) - r_{k,j}(t)) \right) \right).$$

(1.8)

These coefficients are symmetric and satisfy the equality $\sum_{i=1}^{n} M_i \Lambda_{ij} = 0$ in which $M_i$ is the molar mass of component $i$ [23].

The Green-Kubo form of the Onsager coefficients can also be expressed as a function of the molecules velocities as

$$\Lambda_{ij} = \frac{1}{3N} \int_0^\infty dt \left( \sum_{l=1}^{N_i} v_{l,i}(0) \cdot \sum_{k=1}^{N_j} v_{k,j}(t) \right).$$

(1.9)

Here, $v_{l,i}(0)$ is the velocity of the $l$th molecule of component $i$ at time 0 and $v_{k,j}(t)$ is the velocity of the $k$th molecule of component $j$ at time $t$.

$\Lambda_{ii}$ from Eq. (1.9) with $i = j$ can be expressed as

$$\Lambda_{ii} = \frac{1}{3N} \int_0^\infty dt \left( \sum_{l=1}^{N_i} v_{l,i}(0) \cdot \sum_{g=1}^{N_i} v_{g,i}(t) \right)$$

$$= \frac{1}{3N} \int_0^\infty dt \left( \sum_{l=1}^{N_i} v_{l,i}(0) \cdot v_{l,i}(t) \right) + \frac{1}{3N} \int_0^\infty dt \left( \sum_{g=1}^{N_i} \sum_{g \neq l}^{N_i} v_{g,i}(0) \cdot v_{g,i}(t) \right)$$

$$\approx x_i C_{ii} + x_i^2 N C_{ii}^*$$

$$= x_i D_{i,\text{self}} + x_i^2 N C_{ii}^*,$$

(1.10)

in which $C_{ii}$ and $C_{ii}^*$ are the self- and cross- velocity correlations of component $i$, respectively. It is assumed that $N_i$ can be neglected as compared to $N_i^2$.

$\Lambda_{ij}$ from Eq. (1.9) with $i \neq j$ can be expressed as [31]

$$\Lambda_{ij} = \frac{1}{3N} \int_0^\infty dt \left( \sum_{l=1}^{N_i} v_{l,i}(0) \cdot \sum_{k=1}^{N_j} v_{k,j}(t) \right)$$

$$\approx \frac{N_i N_j}{3N} \int_0^\infty dt \left( v_{1,i}(0) \cdot v_{1,j}(t) \right)$$

$$= N x_i x_j C_{ij},$$

(1.11)
The calculation of the correlation functions necessary to obtain the Onsager coefficients can be performed using a conventional algorithm or an algorithm known as the order-n algorithm. [28,32] The latter allows the efficiency of the measurements to be enhanced by using different sampling frequencies.

For binary systems [23], once the Onsager coefficients are determined, one can compute the MS diffusivity with

$$D_{12} = \left[ \frac{x_2}{x_1} \Lambda_{11} + \frac{x_1}{x_2} \Lambda_{22} - 2 \Lambda_{12} \right]. \quad (1.12)$$

The matrix $[B]$ of such systems consists of solely one element which can be calculated with

$$B = \frac{1}{D_{12}}. \quad (1.13)$$

For ternary systems, the expressions relating the Onsager coefficients to the MS diffusivities can be found in [23].

### 1.4.2 Thermodynamic Factors

It is possible to express many thermodynamic properties of mixtures in terms of Kirkwood-Buff (KB) integrals. It is the case for partial molar volumes and activity coefficients, but also for thermodynamics factors [33].

Kirkwood and Buff demonstrated that the density fluctuations in the grand-canonical ensemble are related to volume integrals of radial distribution functions $g_{ij}(r)$ [34,35]. In this context, they defined the KB integrals as

$$G_{ij} = V \frac{\langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle}{\langle N_i \rangle \langle N_j \rangle} - \frac{\delta_{ij}}{c_i} = 4\pi \int_0^\infty [g_{ij}(r) - 1] r^2 dr, \quad (1.14)$$

in which $N_i$ and $N_j$ are the numbers of particles of component $i$ and component $j$ respectively, $\delta_{ij}$ is the Kronecker delta and $c_i$ is the number density of component $i$ ($c_i = \langle N_i \rangle / V$). The symbols $\langle \ldots \rangle$ refer to the ensemble average in the grand-canonical ensemble [18]. The radial distribution function (RDF) can be interpreted as the ratio between the local density at distance $r$ from a central particle and the local density at distance $r$ from a central particle if the system would be an ideal gas. By definition, the RDF of an ideal gas is equal to 1 [36].

While RDFs can be obtained from MD simulations, the computation of the integrals in Eq. (1.14) is not trivial. Three reasons for this can be pointed out [33].

- Since the integration domain extends from zero to infinity, values of the RDFs over an infinite range of distance is needed. However, MD simulation deals only with finite systems.
• The convergence of the RDFs and hence of the KB integrals is extremely slow.

• While the RDFs have to be calculated for open systems, MD simulations are performed only on closed systems.

A way to circumvent the first obstacle is to simply truncate the integrals at an arbitrary distance $R$ [33]:

$$G_{ij}^R = 4\pi \int_0^R [g_{ij}(r) - 1] r^2 dr. \quad (1.15)$$

As all ensembles are equivalent in the classical limit of thermodynamics, $R$ has to be chosen large enough to be as close as possible to this limit and avoid problem of simulating on closed systems. By using a closed system, the integrals do not converge faster.

To facilitate the convergence of the integrals, a smoothing function can be used [33]:

$$G_{ij}^R = 4\pi \int_0^R [g_{ij}(r) - 1] r^2 \left(1 - \frac{3}{2} \left(\frac{r}{R}\right)^2 + \frac{1}{2} \left(\frac{r}{R}\right)^3\right) dr. \quad (1.16)$$

RDFs obtained from simulation do not converge to 1 due to finite-size effects. They can be expressed with a scaling factor for two systems containing $N_1$ and $N_2$ particles respectively:

$$g_{N_1}(r) = g_{\infty}(r) + \frac{c(r)}{N_1} + O\left(\frac{1}{N_1^2}\right), \quad (1.17)$$

$$g_{N_2}(r) = g_{\infty}(r) + \frac{c(r)}{N_2} + O\left(\frac{1}{N_2^2}\right). \quad (1.18)$$

Here, $g_{\infty}(r)$ denotes RDFs of the open systems. From Eqs. (1.17) and (1.18), the function $c(r)$ is

$$c(r) = \frac{g_{N_1} - g_{N_2}}{\frac{1}{N_1} - \frac{1}{N_2}}. \quad (1.19)$$

$g_{\infty}(r)$ is obtained from Eqs. (1.17) and (1.19) using

$$g_{\infty}(r) = g_{N_1}(r) - \frac{c(r)}{N_1}. \quad (1.20)$$

The KB integrals can be expressed finally from Eqs. (1.16) and (1.20) as

$$G_{ij}^R = 4\pi \int_0^R \left[ \left(g_{N_1} - \frac{g_{N_1} - g_{N_2}}{N_1 \left(\frac{1}{N_1} - \frac{1}{N_2}\right)}\right) - 1 \right] r^2 \left(1 - \frac{3}{2} \left(\frac{r}{R}\right)^2 + \frac{1}{2} \left(\frac{r}{R}\right)^3\right) dr. \quad (1.21)$$
For binary systems [34, 37], the thermodynamic factor, $\Gamma$ is calculated by
\[
\Gamma = 1 - x_1 \frac{c_2(G_{11} + G_{22} - 2G_{12})}{1 + x_1 c_2(G_{11} + G_{22} - 2G_{12})}.
\] (1.22)

For ternary systems, the expressions relating the KB coefficients and the thermodynamic factors are given in [19].
Chapter 2

Simulations

2.1 Systems

Alkanolamines are organic compounds that have both an amino- (either \(-\text{NH}_2\), \(-\text{NHR}\) or \(-\text{NR}_2\)) and a hydroxy- \((-\text{OH})\) group. Aqueous solutions of alkanolamine have been used extensively as solvents for the capture of \(\text{CO}_2\) from effluent streams [9]. A primary, a secondary and a tertiary alkanolamine in aqueous solution have been studied. They are monoethanolamine (MEA or \(\text{C}_2\text{H}_7\text{NO}\)), diethanolamine (DEA or \(\text{C}_4\text{H}_{11}\text{NO}_2\)) and methyl-diethanolamine (MDEA or \(\text{C}_5\text{H}_{13}\text{NO}_2\)) respectively. The solvents studied consist of 30 percent by mass of amines. For MEA, the corresponding alkylamine solvent, i.e. ethylamine (\(\text{C}_2\text{H}_7\text{N}\)), has also been simulated to analyze how the \(-\text{OH}\) group of the alkanolamine influences the \(\text{CO}_2\) diffusivity.

Two different \(\text{CO}_2\) concentrations have been simulated for each system to investigate how the diffusivities are affected by the concentration. The maximal percentage of \(\text{CO}_2\) in a system has been determined from the stoichiometry of the reaction occurring between \(\text{CO}_2\) and the amine molecules. For instance, \(\text{CO}_2\) reacts in a 1:2 stoichiometry with a secondary amine, as can be seen in Figure 2.1 [8], leading to a maximum of one \(\text{CO}_2\) molecule per two amine molecules. The stoichiometric ratio is also 1:2 for primary amines but is 1:1 for tertiary amines.

![Figure 2.1: Reaction of \(\text{CO}_2\) with a secondary amine](image)

Figure 2.1: Reaction of \(\text{CO}_2\) with a secondary amine
Table 2.1: Composition of the Studied Systems

<table>
<thead>
<tr>
<th>Solvent</th>
<th>CO$_2$ wt% in the system</th>
<th>N$_2$O wt% in the system</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_7$NO</td>
<td>30wt%</td>
<td>2,6</td>
</tr>
<tr>
<td>C$_4$H$_7$NO$_2$</td>
<td>30wt%</td>
<td>2,4</td>
</tr>
<tr>
<td>C$_5$H$_7$NO$_2$</td>
<td>30wt%</td>
<td>2,6</td>
</tr>
<tr>
<td>C$_2$H$_7$N</td>
<td>30wt%</td>
<td>2</td>
</tr>
</tbody>
</table>

For one of the systems with MEA as solvent, the simulations have also been performed by substituting N$_2$O to CO$_2$ in order to verify the N$_2$O analogy. The composition of the studied systems can be found in Table 2.1.

2.2 Force Fields

A force field is a set of mathematical functions and parameters used to describe the inter- and intra-molecular forces acting on particles. Different force fields have been developed from quantum mechanical calculations and experiments. They differ in their form of the mathematical functions describing the interactions and the value of their parameters which those functions depend on. Some of the most popular force fields are AMBER, GROMOS, CHARMM and OPLS [30].

The potential energy of a system, $E_{total}$, is the sum of all energies arising from bonded and non-bonded interactions. Bonded energy results from intramolecular constraints and non-bonded energy results from both van der Waals and electrostatic forces:

$$E_{total} = E_{bonded} + E_{non-bonded},$$  \hspace{1cm} (2.1)

$$E_{bonded} = E_{bond} + E_{angle} + E_{dihedral},$$  \hspace{1cm} (2.2)

$$E_{non-bonded} = E_{Lennard-Jones} + E_{electrostatic}.$$  \hspace{1cm} (2.3)

**Bond Stretching**

The fluctuations of the distance between two neighboring atoms cause energy changes [30]. This energy is the bond stretching energy, $E_{bond}$. A harmonic potential has been chosen to model the bond stretching:

$$E_{bond} = \frac{k_r}{2} (r - r_0)^2.$$  \hspace{1cm} (2.4)

For a single bond, the force $F_{bond}$ can be derived using $F = -\frac{\partial E}{\partial r}$ and is equal to

$$F_{bond} = -k_r (r - r_0).$$  \hspace{1cm} (2.5)

The parameter $k_r$ is the bond stretching energy constant and $r_0$ as the bond length of lowest energy. Obviously, those two parameters depend on the atoms of the bond.
Angle Bending

The variations of the potential energy also come from the vibrations of the angles constituted by three adjacent atoms. [30] As for bond stretching, a harmonic potential is usually used to represent the potential energy variations arising from angle bending:

\[ E_{\text{angle}} = \frac{k_\theta}{2} (\theta - \theta_0)^2, \]  
\[ F_{\text{angle}} = -k_\theta (\theta - \theta_0). \]  

The constant \( k_\theta \) and the equilibrium angle \( \theta_0 \) are specific to the atoms forming the angle.

Torsion

The dihedral angle potential \( E_{\text{dihedral}} \) which represents the torsional forces inside the molecule, i.e. forces arising from the interactions of four consecutive atoms, is given by

\[ E_{\text{dihedral}} = \sum_{n=0}^{5} C_n \cos^n(\phi - \pi), \]  

where \( \phi \) is the torsional angle and \( C_n \) are constants depending on the atoms forming the dihedral [30].

The OPLS torsion formula is defined as

\[ E_{\text{dihedral}} = \frac{V_1}{2} [1 + \cos(\phi)] + \frac{V_2}{2} [1 - \cos(2\phi)] + \frac{V_3}{2} [1 + \cos(3\phi)] + \frac{V_4}{2} [1 + \cos(4\phi)], \]  

where \( V_1, V_2, V_3 \) and \( V_4 \) are also constants depending on the atoms forming the dihedral and can be related to the \( C_n \) parameters.

Pair Interaction

The repulsive/attractive energy of two non-bonded atoms is described by the Lennard-Jones potential [30]:

\[ E_{\text{Lennard–Jones}} = 4\epsilon_{ij} \left[ \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left( \frac{\sigma_{ij}}{r_{ij}} \right)^{6} \right]. \]  

\( r_{ij} \) is the distance between atoms \( i \) and \( j \), \( \epsilon_{ij} \) is the depth of the potential well and \( \sigma_{ij} \) is the distance at which \( E_{\text{Lennard–Jones}} = 0 \). Figure 2.2 [38] illustrates the Lennard-Jones potential.
Electrostatic Interaction

Due to the charges $q$ on the atoms, electrostatic forces must also be taken into consideration [30]. They are modeled by the Coulomb’s law,

$$E_{\text{electrostatic}} = f \frac{q_i q_j}{\varepsilon_r r_{ij}},$$  \hspace{1cm} (2.11)

in which $f$ is defined as $f = \frac{1}{4\pi \varepsilon_0}$. $\varepsilon_0$ and $\varepsilon_r$ are the vacuum permittivity and the relative permittivity respectively.

The force fields chosen for the simulations are presented in the next section.

2.3 Simulation Details

The simulations were executed with the MD package GROMACS, version 4.5.4. [30]. They were carried out as follows: The initial configuration of the molecules was generated using the Avogadro software and the energy of the system was minimized using the steepest descent algorithm. The system was then equilibrated in the NPT ensemble at a pressure of 1 bar and a temperature of 303 K. The temperature and pressure were kept constant along the simulations by the Nosé-Hoover thermostat and the Parrinello-Rahman barostat respectively. Once the system properties no longer varied with time, the MS diffusivities and thermodynamics factors were computed from simulations in the NVT ensemble. The leap-frog algorithm was used to integrate the equations of motion. Electrostatic interactions were handled by the Particle-Mesh Ewald algorithm. For the computation of the thermodynamic factors, two box sizes were studied for each system, one corresponding to a total number of molecules of the order of 5000 and the other one corresponding to twice this number of molecules. For determining the Maxwell-Stefan diffusivities, a single system size was simulated. The total number of molecules for these simulations was approximately 500. The cut-off radius
applied to truncate the potential was set to 1 nm and a time step of 2 fs was used. Three-dimensional periodic boundary conditions were applied to the cubic simulation boxes in order to avoid finite-size effects and obtain properties of bulk systems.

In the simulations, the OPLS all-atom force field was used for the amine components [39, 40]. The EPM2 and SCP/E force fields were used to model CO$_2$ and H$_2$O respectively [41, 42]. The force field chosen for N$_2$O was developed by La-chet et al. in [43].
Chapter 3

Results and Discussion

The labeling convention used for the results presented in this chapter is given in the following table:

Table 3.1: Labeling convention used for the different components

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary Systems</td>
<td>CO₂ or N₂O</td>
<td>H₂O</td>
<td></td>
</tr>
<tr>
<td>Ternary Systems</td>
<td>CO₂ or N₂O</td>
<td>Amine</td>
<td>H₂O</td>
</tr>
</tbody>
</table>

3.1 Self-Diffusivities

From Eq. (1.7), the self-diffusivity is related to the mean squared displacement of the molecules in the system. The MSD has been computed using the order-\(n\) algorithm [28,32]. Figure 3.1 shows the MSDs as a function of time for the system MEA-H₂O-CO₂ with 6 percent by mass of CO₂ at 303K. It can be observed that three distinct regimes are present. The linear regime after 10 ps can be identified as the diffusive regime. The self-diffusivities are calculated from the MSDs at this diffusive regime.

Figure 3.2 compares the self-diffusivities of the various components in the ternary systems amine-H₂O-CO₂. Their values along with the errors are reported in Appendix A.

The self-diffusivity of CO₂ in MEA solvent is higher when compared to DEA and MDEA solvents. This might result from the fact that the MEA molecules are much smaller than the DEA and MDEA molecules. The self-diffusivity of CO₂ is the lowest in DEA solvent. MEA and DEA have linear chain structures but MDEA has a branched structure. It appears that the self-diffusion of CO₂ is not impeded by the complex molecular geometry of MDEA. The self-diffusivity
Figure 3.1: Mean squared displacements as a function of time for a ternary system MEA-H$_2$O-CO$_2$ with 6wt% of CO$_2$ at 303K calculated using the order-n algorithm. The mean squared displacements become linear after 10 ps and this is the diffusive regime to calculate the self-diffusivities.

Figure 3.2: Self-diffusivities for the different ternary systems amine-H$_2$O-CO$_2$. Ethyl. denotes the ethylamine solvent. The systems denoted with the letter a are the systems containing 2wt% of CO$_2$ while systems denoted with b have a higher CO$_2$ concentration (6wt% for the MEA and MDEA solvent based systems and 4wt% for the DEA solvent based system).
of CO$_2$ in ethylamine solvent is much higher when compared to that with MEA solvent. The presence of hydroxyl group on an amine molecule seems to be an obstacle to diffusion. For all the solvents, the self-diffusivity of the amine molecules is low compared to the one of the CO$_2$ and the water. This results from the fact that the water and CO$_2$ are smaller molecules with a much simpler spatial configuration.

### 3.2 Fick Diffusion Coefficients

To determine Fick diffusivities from molecular simulation, the Maxwell-Stefan diffusivities are first computed. The Onsager coefficients, which are necessary for the computation of the MS diffusivities, are obtained from the correlation functions in Eq. (1.8). The correlation functions have been computed using the order-n algorithm [28, 32]. Figure 3.3 shows the correlation functions as a function of time for the MEA-H$_2$O-CO$_2$ system with 6 percent by mass of CO$_2$ at 303K. As with the MSDs for the self-diffusion coefficients, we also observe three distinct regimes out of which the linear diffusive regime has been identified as the one which is after the timescale of 10 ps. The Onsager coefficients are computed in this diffusive regime. The values of the Onsager coefficients can be found in Appendix B.

The Maxwell-Stefan diffusivities for all the systems are presented in Figure 3.2. Their values are reported in Appendix C.

Similar to the self-diffusivities, the Maxwell-Stefan diffusivities in MEA solvent are higher when compared to DEA and MDEA solvents. The MS diffusivities $D_{12}$ and $D_{23}$ in the DEA and MDEA solvents are similar. The MS diffusivities in the ethylamine solvent are much higher than in the alkanolamine solvents.

In order to compute the Fick diffusivities from the MS diffusivities, the matrix of thermodynamic factors is needed. These $\Gamma_{ij}$ are calculated from the Kirkwood-Buff coefficients. Two different sizes are used to obtain the radial distribution functions for an open system to eliminate the finite size effects as explained in Section 1.4.2. The radial distribution functions have been used to compute the Kirkwood-Buff integrals $G^R$ defined in Eq. (1.21). It is possible to find the value of the KB integrals in the thermodynamic limit $G^\infty$ from $G^R$ as $G^R - G^\infty$ scales with $1/R$ for large $R$. A linear extrapolation of $G^R$ enables $G^\infty$ to be obtained by taking the value corresponding to $1/R \to 0$. The linear regime is identified by plotting $G^R$ as a function of $1/R$. This plot is represented in Figure 3.5 for the MEA-H$_2$O-CO$_2$ system with 6 percent by mass of CO$_2$ at 303K. The value of the KB coefficients are reported in Appendix D.
Figure 3.3: Correlation functions as a function of time for the ternary system MEA-H$_2$O-CO$_2$ with 6wt% of CO$_2$ at 303K calculated using the order-n algorithm. The diffusive regime for this system can be found after 10 ps and the MS diffusion coefficients are calculated beyond 10 ps.

Figure 3.4: Maxwell-Stefan diffusivities $D_{ij}$ for the different systems at 303K. Ethyl. denotes the ethylamine solvent. The systems denoted with the letter a are the systems containing 2wt% of CO$_2$ while systems denoted with b have a higher CO$_2$ concentration (6wt% for the MEA and MDEA solvent based systems and 4wt% for the DEA solvent based system).
Figure 3.5: Kirkwood-Buff integrals $G_{ij}$ as a function of $1/R$ for a ternary MEA-H$_2$O-CO$_2$ system with 6wt% of CO$_2$ at 303K. The data between the two dotted vertical lines have been used to extrapolate and obtain the Kirkwood-Buff coefficients in the thermodynamic limit.

The thermodynamic factors for the different solvent systems are then computed and are shown in Figure 3.6. Their values can be found in Appendix E.

In case of infinite dilution, the matrix of thermodynamic factors reduces to

$$\Gamma_{ii}^{x_i \to 0} = 1,$$

$$\Gamma_{ij, i \neq j}^{x_i \to 0} = 0.$$  

The mole fraction of CO$_2$ in the systems are given in Table 3.2.

<table>
<thead>
<tr>
<th>wt% CO$_2$</th>
<th>MEA</th>
<th>MEA</th>
<th>DEA</th>
<th>DEA</th>
<th>MDEA</th>
<th>MDEA</th>
<th>Ethylamine</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>6</td>
<td>2</td>
<td>4</td>
<td>2</td>
<td>6</td>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>$x_{CO_2}$</td>
<td>0.0105</td>
<td>0.0321</td>
<td>0.0110</td>
<td>0.0222</td>
<td>0.0111</td>
<td>0.0339</td>
<td>0.0101</td>
</tr>
</tbody>
</table>
Figure 3.6: Thermodynamic factors $\Gamma_{ij}$ for the different systems at 303K. (1)-CO$_2$, (2)-amine, (3)-H$_2$O. Ethyl. denotes the ethylamine solvent. The systems denoted with the letter a are the systems containing 2wt% of CO$_2$ while systems denoted with b have a higher CO$_2$ concentration (6wt% for the MEA and MDEA solvent based systems and 4wt% for the DEA solvent based system).

For the systems with an alkanolamine solvent and 2 percent by mass of CO$_2$, the mole fraction of CO$_2$, $x_{CO_2}$, is close to 1%. From the value of the thermodynamic factors, one can conclude that those systems are ideal. This is not the case for the alkanolamine solvent systems with a higher CO$_2$ concentration. Their $\Gamma_{11}$ and $\Gamma_{12}$ deviate significantly from 1 and 0 respectively.

Combining the values of the MS diffusivities and the thermodynamic factors allows to determine the Fick diffusion coefficients. The Fick diffusivities are compared in Figure 3.7 and their values are shown in Appendix F.

The Fick diffusion coefficients, just like the MS diffusivities, exhibit higher values for the systems containing MEA than for the systems containing one of the two other alkanolamines. Comparing the values of the Fick diffusion coefficients for the DEA and MDEA solvent based systems leads to the conclusion that the geometry of the MDEA molecules does not affect significantly the diffusion. As already observed for the self-diffusion coefficients and the Maxwell-Stefan diffusivities, the presence of OH- groups in the amine molecule obstructs the diffusion.

Although hydroxyl groups have an unfavourable effect on diffusion, it should not be forgotten that they also provide advantages while looking at the CO$_2$ ab-
Figure 3.7: Fick diffusion coefficients $D_{ij}$ for the different solvent systems at 303K. (1)- CO$_2$, (2)-amine, (3)-H$_2$O. Ethyl. denotes the ethylamine solvent. The systems denoted with the letter a are the systems containing 2wt% of CO$_2$ while systems denoted with b have a higher CO$_2$ concentration (6wt% for the MEA and MDEA solvent based systems and 4wt% for the DEA solvent based system).

... sorption process in its entirety. They allow the reduction of the vapor pressure, help to increase the solubility of the amine in water and the CO$_2$ capacity in the solvent [44, 45]. They will also influence the reactions occurring during the CO$_2$ absorption process.

### 3.3 N$_2$O Analogy

In order to validate the N$_2$O analogy, the diffusion of CO$_2$ in MEA has been computed in two different ways.

- **Approach 1:** Without the Analogy
  $(D_{CO_2})_{MEA}$ has been directly computed from simulating a system containing CO$_2$ with MEA in aqueous solution as solvent. There is no reaction present between CO$_2$ and MEA during the simulations.

- **Approach 2:** With the Analogy
  $(D_{CO_2})_{MEA}$ has been estimated using the N$_2$O analogy,
  \[
  (D_{CO_2})_{MEA} = (D_{N_2O})_{MEA} \left( \frac{D_{CO_2}}{D_{N_2O}} \right)_{water},
  \]
  (3.3)
where \((D_{N_2O})_{MEA}\) has been computed from simulating a MEA-H\textsubscript{2}O-N\textsubscript{2}O system, \((D_{CO_2})_{water}\) from simulating a H\textsubscript{2}O-CO\textsubscript{2} system and \((D_{N_2O})_{water}\) from simulating a H\textsubscript{2}O-N\textsubscript{2}O system.

The results are presented in Table 3.3.

Table 3.3: CO\textsubscript{2} diffusivities computed with and without the analogy

<table>
<thead>
<tr>
<th>without the Analogy</th>
<th>With the Analogy</th>
</tr>
</thead>
<tbody>
<tr>
<td>((D_{CO_2})_{MEA}) (10^{-9})m\textsuperscript{2}/s</td>
<td>((D_{CO_2})_{MEA}) (10^{-9})m\textsuperscript{2}/s</td>
</tr>
<tr>
<td>MEA 2wt% of CO\textsubscript{2}</td>
<td>1.6543 ± 0.0026</td>
</tr>
<tr>
<td>MEA 6wt% of CO\textsubscript{2}</td>
<td>1.6752 ± 0.0011</td>
</tr>
</tbody>
</table>

\((D_{CO_2})_{MEA}\) has also been computed using the N\textsubscript{2}O analogy using the experimental value for \((D_{N_2O})_{MEA}\) found in [46] and the correlations developed in [10] to find the values of \((D_{CO_2})_{water}\) and \((D_{N_2O})_{water}\) at 303K. \((D_{N_2O})_{MEA}\) corresponds to the infinite dilution of CO\textsubscript{2} in MEA. It gives \((D_{CO_2})_{MEA} = 1.6610 \times 10^{-9}\)m\textsuperscript{2}/s.

We find that the values of the diffusion coefficient of CO\textsubscript{2} in MEA from experiments and simulation are in agreement with each other for the concentrations near infinite dilution. A systematic validation of the analogy would require to study how accurate the analogy predicts the \((D_{CO_2})_{amine}\) dependence on the temperature and pressure of the system, the amine concentration in solution, the CO\textsubscript{2} concentration in the system and this for different amine solvents as well.
Conclusion

The study of the self-diffusion pointed out that in any system constituted of CO$_2$, amine and water, the self-diffusion of the amine is slow compared to the self-diffusion of the two other components. This can be explained by the fact that the amine molecules have a bigger and more complex structure that impedes their motion.

Self-diffusivities, Maxwell-Stefan diffusivities and Fick diffusion coefficients exhibit similar trends.

- Among the alkanolamine solvents, the diffusivity of CO$_2$ is the highest in MEA. This could be related to the spatial configuration of the MEA molecule which is smaller than the one of DEA and MDEA.

- The diffusion in MDEA solvent is not significantly affected by the branched molecular geometry of MDEA that could have generated serious steric effects.

- The presence of hydroxyl groups on an amine molecule is an obstacle to diffusion. The OH- group is responsible for interactions that affect the diffusive transport. This explains the high value of all the diffusivities in the ethylamine solvent as compared as in the alkanolamine solvents. This could also be the reason why MEA, which carries only one hydroxyl group, yields to higher diffusivities than DEA and MDEA which carry two of them.

The hydroxyl group effect on the diffusive transport appears to be dominant compared to the influence of the molecular geometry of the amine.

Further investigations could include the study of other solvent compositions, temperatures, pressures and higher CO$_2$ concentrations in the system. Research on the effect of other substitutive groups on the diffusion can also be carried out. Finally, it is primordial to conduct research towards a better understanding of the reactions occurring when CO$_2$ is absorbed into amine solvents to understand the mass transport process in its entirety.
Values in agreement with the N$_2$O analogy were found from simulation. However, to investigate the limitations of the analogy, a rigorous study should be performed for different temperatures, pressures, system compositions and amine types.
Bibliography


Appendix A

Self-Diffusivities

The self-diffusivities are given in m²s⁻¹.

Table A.1: Self-diffusivities and errors from linear regression

<table>
<thead>
<tr>
<th></th>
<th></th>
<th>10⁹D₁,₁₅</th>
<th>10⁹D₂,₁₅</th>
<th>10⁹D₃,₁₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O</td>
<td>CO₂</td>
<td>2.7942</td>
<td>1.6874E-02</td>
<td>0.6039%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8287</td>
<td>1.8532E-04</td>
<td>0.0066%</td>
</tr>
<tr>
<td>H₂O</td>
<td>N₂O</td>
<td>2.4736</td>
<td>1.3132E-02</td>
<td>0.5309%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.8448</td>
<td>3.8490E-04</td>
<td>0.0135%</td>
</tr>
<tr>
<td>C₂H₇NO</td>
<td>2wt% of CO₂</td>
<td>1.6543</td>
<td>2.5780E-03</td>
<td>0.1558%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7946</td>
<td>4.3475E-04</td>
<td>0.0547%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.5760</td>
<td>1.6745E-04</td>
<td>0.0106%</td>
</tr>
<tr>
<td>C₂H₇NO</td>
<td>6wt% of CO₂</td>
<td>1.6752</td>
<td>1.1223E-03</td>
<td>0.0670%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7401</td>
<td>1.9382E-04</td>
<td>0.0262%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4920</td>
<td>3.2611E-04</td>
<td>0.0219%</td>
</tr>
<tr>
<td>C₂H₇NO</td>
<td>2wt% of N₂O</td>
<td>1.4435</td>
<td>1.0313E-03</td>
<td>0.0714%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7116</td>
<td>2.6204E-04</td>
<td>0.0368%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4673</td>
<td>1.7778E-04</td>
<td>0.0121%</td>
</tr>
<tr>
<td>C₂H₇NO</td>
<td>6wt% of N₂O</td>
<td>1.6036</td>
<td>1.1709E-03</td>
<td>0.0730%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7540</td>
<td>6.7019E-04</td>
<td>0.0889%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.4948</td>
<td>1.6491E-04</td>
<td>0.0110%</td>
</tr>
<tr>
<td>Compound</td>
<td>CO2 (%)</td>
<td>$^{10}D_{1,\text{self}}$</td>
<td>$^{10}D_{2,\text{self}}$</td>
<td>$^{10}D_{3,\text{self}}$</td>
</tr>
<tr>
<td>--------------</td>
<td>---------</td>
<td>--------------------------</td>
<td>--------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{11}$NO$_2$ 2wt% of CO$_2$</td>
<td>1.2349 ± 1.9729E-03 (0.1598%)</td>
<td>0.3457 ± 2.7782E-03 (0.8036%)</td>
<td>1.2556 ± 5.0983E-04 (0.0406%)</td>
<td></td>
</tr>
<tr>
<td>C$<em>4$H$</em>{11}$NO$_2$ 4wt% of CO$_2$</td>
<td>1.1295 ± 2.4261E-03 (0.2148%)</td>
<td>0.3139 ± 3.1860E-03 (1.0151%)</td>
<td>1.1708 ± 2.5346E-04 (0.0216%)</td>
<td></td>
</tr>
<tr>
<td>C$<em>5$H$</em>{13}$NO$_2$ 2wt% of CO$_2$</td>
<td>1.3378 ± 3.9085E-03 (0.2922%)</td>
<td>0.3408 ± 3.3661E-03 (0.9876%)</td>
<td>1.3291 ± 3.9983E-04 (0.0301%)</td>
<td></td>
</tr>
<tr>
<td>C$<em>5$H$</em>{13}$NO$_2$ 6wt% of CO$_2$</td>
<td>1.4619 ± 2.4758E-03 (0.1694%)</td>
<td>0.3283 ± 6.1432E-04 (0.1871%)</td>
<td>1.3028 ± 7.1641E-04 (0.0550%)</td>
<td></td>
</tr>
<tr>
<td>C$_2$H$_7$N 2wt% of CO$_2$</td>
<td>2.3106 ± 1.9988E-03 (0.0865%)</td>
<td>1.1464 ± 4.2844E-04 (0.0374%)</td>
<td>1.6524 ± 2.0521E-04 (0.0124%)</td>
<td></td>
</tr>
</tbody>
</table>
Appendix B

Onsager Coefficients

The Onsager coefficients are given in nm²ps⁻¹.

Table B.1: Onsager coefficients and errors from linear regression

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt% of CO₂</th>
<th>( \Lambda_{11} )</th>
<th>±</th>
<th>( \Lambda_{12} )</th>
<th>±</th>
<th>( \Lambda_{13} )</th>
<th>±</th>
<th>( \Lambda_{22} )</th>
<th>±</th>
<th>( \Lambda_{23} )</th>
<th>±</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₂H₇NO</td>
<td>2%</td>
<td>1.7505E-05</td>
<td>± 1.7453E-07</td>
<td>(0.9970%)</td>
<td>6.1552E-05</td>
<td>± 2.1204E-07</td>
<td>(0.3445%)</td>
<td>7.4357E-04</td>
<td>± 2.5627E-06</td>
<td>(0.3447%)</td>
<td>-2.9322E-06</td>
</tr>
<tr>
<td></td>
<td>6%</td>
<td>5.3418E-05</td>
<td>± 1.5888E-07</td>
<td>(0.2974%)</td>
<td>5.6812E-05</td>
<td>± 2.0738E-07</td>
<td>(0.3650%)</td>
<td>7.7460E-04</td>
<td>± 7.1806E-08</td>
<td>(0.6142%)</td>
<td>-1.1692E-05</td>
</tr>
<tr>
<td>C₄H₁₁NO₂</td>
<td>2%</td>
<td>1.4600E-05</td>
<td>± 4.3566E-08</td>
<td>(0.2984%)</td>
<td>2.1287E-05</td>
<td>± 2.2719E-07</td>
<td>(1.0673%)</td>
<td>6.3751E-04</td>
<td>± 1.2582E-06</td>
<td>(0.1974%)</td>
<td>-1.5730E-06</td>
</tr>
<tr>
<td></td>
<td>6%</td>
<td>2.1287E-05</td>
<td>± 2.2719E-07</td>
<td>(1.0673%)</td>
<td>6.3751E-04</td>
<td>± 1.2582E-06</td>
<td>(0.1974%)</td>
<td>-1.5730E-06</td>
<td>± 4.2736E-08</td>
<td>(2.7169%)</td>
<td>-2.4626E-05</td>
</tr>
<tr>
<td>Compound</td>
<td>% CO₂</td>
<td>( \Lambda_{11} )</td>
<td>( \Lambda_{12} )</td>
<td>( \Lambda_{13} )</td>
<td>( \Lambda_{22} )</td>
<td>( \Lambda_{23} )</td>
<td>( \Lambda_{33} )</td>
<td>Percentage</td>
<td></td>
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</tr>
<tr>
<td>( \ce{C4H11NO2} )</td>
<td>4wt%</td>
<td>2.2704E-05 ± 6.2136E-07</td>
<td>2.3802E-05 ± 2.1274E-07</td>
<td>5.8406E-04 ± 1.8241E-06</td>
<td>-3.1635E-06 ± 9.0161E-08</td>
<td>-3.6192E-05 ± 2.5742E-07</td>
<td>5.8406E-04 ± 1.8241E-06</td>
<td>2.7367%</td>
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<td></td>
<td>1.5129E-05 ± 1.9003E-08</td>
<td>2.4799E-05 ± 2.0501E-07</td>
<td>7.4351E-04 ± 1.3511E-06</td>
<td>-1.3562E-06 ± 1.7771E-08</td>
<td>-2.7776E-05 ± 1.0125E-07</td>
<td>7.4351E-04 ± 1.3511E-06</td>
<td>0.1256%</td>
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<tr>
<td>( \ce{C5H13NO2} )</td>
<td>6wt%</td>
<td>4.7832E-05 ± 3.4402E-08</td>
<td>2.9332E-05 ± 2.8809E-07</td>
<td>8.5964E-04 ± 1.2129E-06</td>
<td>-4.4793E-06 ± 1.1548E-08</td>
<td>-8.6166E-05 ± 7.5688E-08</td>
<td>8.5964E-04 ± 1.2129E-06</td>
<td>0.0719%</td>
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</tr>
<tr>
<td>( \ce{C2H7N} )</td>
<td>2wt%</td>
<td>2.4643E-05 ± 8.6438E-08</td>
<td>1.3850E-04 ± 9.6452E-08</td>
<td>9.7990E-04 ± 3.8975E-07</td>
<td>-3.1410E-06 ± 3.3764E-08</td>
<td>-5.2675E-05 ± 1.6845E-07</td>
<td>9.7990E-04 ± 3.8975E-07</td>
<td>0.3508%</td>
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</table>
Appendix C

Maxwell-Stefan Diffusivities

The Maxwell-Stefan diffusivities are given in m$^2$s$^{-1}$.

Table C.1: Maxwell-Stefan diffusivities and errors from linear regression

<table>
<thead>
<tr>
<th></th>
<th>2wt% of CO$_2$</th>
<th>6wt% of CO$_2$</th>
<th>2wt% of CO$_2$</th>
<th>4wt% of CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_7$NO</td>
<td>$10^9D_{12}$</td>
<td>0.3677 ± 2.8145E-02 (7.6544%)</td>
<td>0.3000 ± 1.1893E-02 (3.9641%)</td>
<td>0.3000 ± 1.1893E-02 (3.9641%)</td>
</tr>
<tr>
<td></td>
<td>$10^9D_{13}$</td>
<td>1.2644 ± 5.9493E-02 (4.7054%)</td>
<td>1.8531 ± 4.0995E-02 (2.2123%)</td>
<td>1.8531 ± 4.0995E-02 (2.2123%)</td>
</tr>
<tr>
<td></td>
<td>$10^9D_{23}$</td>
<td>0.5593 ± 5.3974E-03 (0.9650%)</td>
<td>0.5413 ± 4.6700E-03 (0.8627%)</td>
<td>0.5413 ± 4.6700E-03 (0.8627%)</td>
</tr>
<tr>
<td>C$_2$H$_7$NO</td>
<td>$10^9D_{12}$</td>
<td>0.4845 ± 2.0105E-02 (4.1494%)</td>
<td>0.7008 ± 1.5389E-02 (2.1958%)</td>
<td>0.7008 ± 1.5389E-02 (2.1958%)</td>
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<tr>
<td></td>
<td>$10^9D_{13}$</td>
<td>2.5362 ± 1.0277E-01 (4.0522%)</td>
<td>2.2907 ± 2.8399E-02 (1.2398%)</td>
<td>2.2907 ± 2.8399E-02 (1.2398%)</td>
</tr>
<tr>
<td></td>
<td>$10^9D_{23}$</td>
<td>0.9895 ± 5.3617E-03 (0.5419%)</td>
<td>0.9032 ± 4.3876E-03 (0.4858%)</td>
<td>0.9032 ± 4.3876E-03 (0.4858%)</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{11}$NO$_2$</td>
<td>$10^9D_{12}$</td>
<td>0.3677 ± 2.8145E-02 (7.6544%)</td>
<td>0.3000 ± 1.1893E-02 (3.9641%)</td>
<td>0.3000 ± 1.1893E-02 (3.9641%)</td>
</tr>
<tr>
<td></td>
<td>$10^9D_{13}$</td>
<td>1.2644 ± 5.9493E-02 (4.7054%)</td>
<td>1.8531 ± 4.0995E-02 (2.2123%)</td>
<td>1.8531 ± 4.0995E-02 (2.2123%)</td>
</tr>
<tr>
<td></td>
<td>$10^9D_{23}$</td>
<td>0.5593 ± 5.3974E-03 (0.9650%)</td>
<td>0.5413 ± 4.6700E-03 (0.8627%)</td>
<td>0.5413 ± 4.6700E-03 (0.8627%)</td>
</tr>
<tr>
<td>Compound</td>
<td>CO₂ %</td>
<td>$10^9D_{12}$</td>
<td>$10^9D_{13}$</td>
<td>$10^9D_{23}$</td>
</tr>
<tr>
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</tr>
<tr>
<td>C₅H₁₃NO₂</td>
<td>2 wt%</td>
<td>0.2909 ± 5.6797E-03</td>
<td>1.8698 ± 1.8495E-02</td>
<td>0.6501 ± 4.1912E-03</td>
</tr>
<tr>
<td>C₅H₁₃NO₂</td>
<td>6 wt%</td>
<td>0.3638 ± 4.0041E-03</td>
<td>1.9699 ± 9.4446E-03</td>
<td>0.7450 ± 5.7672E-03</td>
</tr>
<tr>
<td>C₂H₇N</td>
<td>2 wt%</td>
<td>0.6059 ± 6.0991E-03</td>
<td>5.4432 ± 1.1978E-01</td>
<td>1.6729 ± 2.2326E-03</td>
</tr>
</tbody>
</table>

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Appendix D

Kirkwood-Buff Coefficients

The Kirkwood-Buff coefficients are given in nm$^{-3}$.

Table D.1: Kirkwood-Buff coefficients and errors from linear regression

<table>
<thead>
<tr>
<th>Compound</th>
<th>wt% of CO$_2$</th>
<th>$G_{11}$</th>
<th>$G_{22}$</th>
<th>$G_{33}$</th>
<th>$G_{12}$</th>
<th>$G_{13}$</th>
<th>$G_{23}$</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_2H_7NO$</td>
<td>2</td>
<td>-5.9450E-02</td>
<td>-1.3386E-01</td>
<td>-5.4880E-03</td>
<td>-2.0507E-03</td>
<td>-7.8477E-02</td>
<td>-8.2158E-02</td>
<td>1.8916%</td>
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<tr>
<td></td>
<td></td>
<td>± 1.1246E-03</td>
<td>± 9.0219E-05</td>
<td>± 4.6903E-06</td>
<td>± 1.8832E-04</td>
<td>± 5.2194E-05</td>
<td>± 1.8874E-05</td>
<td>0.0674%</td>
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<tr>
<td></td>
<td>6</td>
<td>3.8866E-01</td>
<td>-1.2794E-01</td>
<td>7.8150E-03</td>
<td>1.6248E-02</td>
<td>-1.3611E-01</td>
<td>-9.3945E-02</td>
<td>0.2561%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>± 9.9521E-04</td>
<td>± 3.7895E-05</td>
<td>± 4.0343E-05</td>
<td>± 1.5932E-04</td>
<td>± 1.8042E-04</td>
<td>± 5.1349E-05</td>
<td>0.0296%</td>
</tr>
<tr>
<td>$C_4H_{11}NO_2$</td>
<td>2</td>
<td>-5.4282E-02</td>
<td>-1.4968E-01</td>
<td>1.7417E-02</td>
<td>2.3017E-04</td>
<td>-7.7790E-02</td>
<td>-1.4410E-01</td>
<td>0.8295%</td>
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<tr>
<td></td>
<td></td>
<td>± 4.5025E-04</td>
<td>± 3.6673E-05</td>
<td>± 6.2784E-05</td>
<td>± 2.6298E-04</td>
<td>± 7.7346E-05</td>
<td>± 1.7387E-04</td>
<td>0.0245%</td>
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</tr>
<tr>
<td>Compound</td>
<td>wt% of CO₂</td>
<td>G_{11}</td>
<td>G_{22}</td>
<td>G_{33}</td>
<td>G_{12}</td>
<td>G_{13}</td>
<td>G_{23}</td>
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</tr>
<tr>
<td>C₄H₁₁NO₂</td>
<td>4wt%</td>
<td>9.1728E-02 ± 8.4197E-05 (0.0918%)</td>
<td>-1.5132E-01 ± 8.7201E-05 (0.0576%)</td>
<td>2.2610E-02 ± 6.9152E-05 (0.3058%)</td>
<td>1.1091E-02 ± 2.0318E-04 (1.8319%)</td>
<td>-9.2892E-02 ± 6.6462E-05 (0.0715%)</td>
<td>-1.5287E-01 ± 1.8351E-04 (0.1200%)</td>
<td></td>
</tr>
<tr>
<td>C₅H₁₃NO₂</td>
<td>2wt%</td>
<td>9.0996E-02 ± 2.3026E-05 (0.0253%)</td>
<td>-1.1806E-01 ± 2.8669E-04 (0.2428%)</td>
<td>4.2095E-02 ± 1.1616E-04 (0.2759%)</td>
<td>6.1443E-02 ± 5.5221E-04 (0.8987%)</td>
<td>-1.0620E-01 ± 1.5420E-04 (0.1452%)</td>
<td>-1.9761E-01 ± 3.1948E-04 (0.1617%)</td>
<td></td>
</tr>
<tr>
<td>C₅H₁₃NO₂</td>
<td>6wt%</td>
<td>3.6226E-01 ± 1.0326E-03 (0.2850%)</td>
<td>-7.1873E-02 ± 7.3851E-04 (1.0275%)</td>
<td>7.0459E-02 ± 2.3060E-04 (0.3273%)</td>
<td>1.2061E-01 ± 8.7321E-04 (0.7240%)</td>
<td>-1.7799E-01 ± 3.9494E-04 (0.2219%)</td>
<td>-2.3600E-01 ± 5.3994E-04 (0.2288%)</td>
<td></td>
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<tr>
<td>C₂H₇N</td>
<td>2wt%</td>
<td>1.0438E+00 ± 2.6661E-03 (0.2554%)</td>
<td>-3.0797E-02 ± 5.1380E-04 (1.6684%)</td>
<td>8.2422E-02 ± 1.1862E-04 (0.1439%)</td>
<td>2.4643E-01 ± 1.0717E-03 (0.4349%)</td>
<td>-3.4227E-01 ± 5.4088E-04 (0.1580%)</td>
<td>-1.6845E-01 ± 2.9301E-04 (0.1739%)</td>
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</tr>
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</table>
Appendix E

Thermodynamic Factors

Table E.1: Thermodynamic factors and errors from linear regression

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight % of CO₂</th>
<th>( \Gamma )</th>
<th>Value</th>
<th>Error</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_2\text{H}_7\text{NO} )</td>
<td>2wt%</td>
<td>( \Gamma_{11} )</td>
<td>9.9485E-01</td>
<td>± 1.2654E-03</td>
<td>(0.1272%)</td>
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<td>( \Gamma_{12} )</td>
<td>-3.8336E-02</td>
<td>± 7.9727E-05</td>
<td>(0.2080%)</td>
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<td>( \Gamma_{21} )</td>
<td>-3.6921E-01</td>
<td>± 1.6858E-03</td>
<td>(0.4566%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \Gamma_{22} )</td>
<td>9.5768E-01</td>
<td>± 1.2209E-03</td>
<td>(0.1275%)</td>
</tr>
<tr>
<td>( \text{C}_2\text{H}_7\text{NO} )</td>
<td>6wt%</td>
<td>( \Gamma_{11} )</td>
<td>7.1035E-01</td>
<td>± 2.1576E-03</td>
<td>(0.3037%)</td>
</tr>
<tr>
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<td>( \Gamma_{12} )</td>
<td>-1.2038E-01</td>
<td>± 4.6779E-04</td>
<td>(0.3886%)</td>
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<tr>
<td></td>
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<td>( \Gamma_{21} )</td>
<td>-3.5040E-01</td>
<td>± 3.2451E-03</td>
<td>(0.9261%)</td>
</tr>
<tr>
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<td>( \Gamma_{22} )</td>
<td>9.3369E-01</td>
<td>± 3.1373E-03</td>
<td>(0.3360%)</td>
</tr>
<tr>
<td>( \text{C}<em>4\text{H}</em>{11}\text{NO} )</td>
<td>2wt%</td>
<td>( \Gamma_{11} )</td>
<td>9.9122E-01</td>
<td>± 1.4637E-03</td>
<td>(0.1477%)</td>
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<tr>
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<td>( \Gamma_{12} )</td>
<td>-5.0415E-02</td>
<td>± 1.3938E-04</td>
<td>(0.2765%)</td>
</tr>
<tr>
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<td>( \Gamma_{21} )</td>
<td>-3.0461E-01</td>
<td>± 1.2157E-03</td>
<td>(0.3991%)</td>
</tr>
<tr>
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<td>( \Gamma_{22} )</td>
<td>8.1790E-01</td>
<td>± 8.8602E-04</td>
<td>(0.1083%)</td>
</tr>
<tr>
<td>( \text{C}<em>4\text{H}</em>{11}\text{NO} )</td>
<td>4wt%</td>
<td>( \Gamma_{11} )</td>
<td>9.0577E-01</td>
<td>± 1.4247E-03</td>
<td>(0.1573%)</td>
</tr>
<tr>
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<td>( \Gamma_{12} )</td>
<td>-1.0409E-01</td>
<td>± 2.5748E-04</td>
<td>(0.2474%)</td>
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<td>( \Gamma_{21} )</td>
<td>-3.0455E-01</td>
<td>± 1.0571E-03</td>
<td>(0.3471%)</td>
</tr>
<tr>
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<td>( \Gamma_{22} )</td>
<td>8.2463E-01</td>
<td>± 8.8191E-04</td>
<td>(0.1069%)</td>
</tr>
<tr>
<td>Compound</td>
<td>CO₂ Concentration</td>
<td>( \Gamma_1 )</td>
<td>( \Gamma_2 )</td>
<td>( \Gamma_3 )</td>
<td>( \Gamma_4 )</td>
</tr>
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</tr>
<tr>
<td>C₅H₁₃NO₂ 2wt% of CO₂</td>
<td>9.5602E-01 ± 2.2770E-03 (0.2382%)</td>
<td>-7.0470E-02 ± 2.3591E-04 (0.3348%)</td>
<td>-3.7736E-01 ± 1.8391E-03 (0.4874%)</td>
<td>7.2004E-01 ± 1.0664E-03 (0.1481%)</td>
<td></td>
</tr>
<tr>
<td>C₅H₁₃NO₂ 6wt% of CO₂</td>
<td>7.2674E-01 ± 4.4362E-03 (0.6104%)</td>
<td>-2.0762E-01 ± 1.4915E-03 (0.7184%)</td>
<td>-3.5076E-01 ± 3.4425E-03 (0.9814%)</td>
<td>7.2458E-01 ± 3.9262E-03 (0.5419%)</td>
<td></td>
</tr>
<tr>
<td>C₂H₇N 2wt% of CO₂</td>
<td>8.3849E-01 ± 6.4813E-03 (0.7730%)</td>
<td>-7.5079E-02 ± 3.1185E-04 (0.4154%)</td>
<td>-9.7362E-01 ± 2.3328E-02 (2.3960%)</td>
<td>5.4987E-01 ± 3.6693E-03 (0.6673%)</td>
<td></td>
</tr>
</tbody>
</table>
Appendix F

Fick Diffusion Coefficients

The Fick diffusion coefficients are given in m$^2$s$^{-1}$.

Table F.1: Fick diffusion coefficients and errors from linear regression

<table>
<thead>
<tr>
<th>Compound</th>
<th>CO$_2$ Concentration</th>
<th>$10^9D_{11}$</th>
<th>Error</th>
<th>Relative Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_2$H$_7$NO</td>
<td>2wt% of CO$_2$</td>
<td>1.7109</td>
<td>± 1.9861E-02</td>
<td>(1.1609%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0379</td>
<td>± 1.9483E-03</td>
<td>(5.1328%)</td>
</tr>
<tr>
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<td></td>
<td>0.1654</td>
<td>± 1.6073E-02</td>
<td>(9.7171%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.9330</td>
<td>± 5.5611E-03</td>
<td>(0.5960%)</td>
</tr>
<tr>
<td>C$_2$H$_7$NO</td>
<td>6wt% of CO$_2$</td>
<td>1.2887</td>
<td>± 8.6713E-03</td>
<td>(0.6729%)</td>
</tr>
<tr>
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<td></td>
<td>0.1727</td>
<td>± 2.9977E-03</td>
<td>(1.7358%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2734</td>
<td>± 7.5482E-03</td>
<td>(2.7609%)</td>
</tr>
<tr>
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<td></td>
<td>0.8302</td>
<td>± 6.5765E-03</td>
<td>(0.7921%)</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{11}$NO</td>
<td>2wt% of CO$_2$</td>
<td>1.3541</td>
<td>± 6.5152E-03</td>
<td>(0.4811%)</td>
</tr>
<tr>
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<td>0.0507</td>
<td>± 1.1447E-03</td>
<td>(2.2568%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0899</td>
<td>± 7.1557E-03</td>
<td>(7.9603%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4361</td>
<td>± 4.0797E-03</td>
<td>(0.9354%)</td>
</tr>
<tr>
<td>C$<em>4$H$</em>{11}$NO</td>
<td>4wt% of CO$_2$</td>
<td>0.9788</td>
<td>± 2.7499E-02</td>
<td>(2.8095%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0921</td>
<td>± 4.6980E-03</td>
<td>(5.1013%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1348</td>
<td>± 7.9183E-03</td>
<td>(5.8754%)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4528</td>
<td>± 4.2328E-03</td>
<td>(0.9348%)</td>
</tr>
<tr>
<td>Component</td>
<td>CO₂ Concentration</td>
<td>$^{10}D_{ij}$</td>
<td>Error</td>
<td>Error Percentage</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------</td>
<td>--------------</td>
<td>-------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>C₅H₁₃NO₂</td>
<td>2wt% of CO₂</td>
<td>1.3426 ± 5.3190E-03</td>
<td>0.3962%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.0787 ± 8.5735E-04</td>
<td>1.0889%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1441 ± 5.1611E-03</td>
<td>3.5823%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.4560 ± 3.5621E-03</td>
<td>0.7811%</td>
<td></td>
</tr>
<tr>
<td>C₅H₁₃NO₂</td>
<td>6wt% of CO₂</td>
<td>1.1149 ± 8.3485E-03</td>
<td>0.7488%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.2648 ± 3.3325E-03</td>
<td>1.2586%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1861 ± 5.1495E-03</td>
<td>2.7666%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5056 ± 6.7015E-03</td>
<td>1.3255%</td>
<td></td>
</tr>
<tr>
<td>C₂H₇N</td>
<td>2wt% of CO₂</td>
<td>2.0739 ± 2.5852E-02</td>
<td>1.2466%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.1571 ± 1.9450E-03</td>
<td>1.2382%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.0795 ± 5.0029E-02</td>
<td>4.6345%</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.8644 ± 7.5651E-03</td>
<td>0.8752%</td>
<td></td>
</tr>
</tbody>
</table>