Timescales for the Development of Thermodynamic Equilibrium in Hydrocarbon Reservoirs

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A thesis submitted for the degree of

Doctor of Philosophy

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Declaration of Originality

I declare that this thesis, Timescales for the Development of Thermodynamic Equilibrium in Hydrocarbon Reservoirs, is entirely my own work under the supervision of Prof. Ann Muggeridge, Prof. Velisa Vesovic and Dr. Nicolas Riesco. The work was performed in the Department of Earth Science and Engineering at Imperial College London. All published and unpublished material used in the thesis has been given full acknowledgment. This work has not been previously submitted, in whole or in part, to any other academic institution for a degree, diploma, or any other qualification.

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<th>Description</th>
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<td>tortuosity factor</td>
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<td>$c_e$</td>
<td>effective compressibility</td>
<td>Pa$^{-1}$</td>
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<td>$c_p$</td>
<td>heat capacity at constant pressure</td>
<td>J.K$^{-1}$</td>
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<td>$c$</td>
<td>molar concentration per unit volume of the mixture</td>
<td>mol. m$^{-3}$</td>
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<td>molar concentration of component $i$ in the mixture</td>
<td>mol. m$^{-3}$</td>
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<td>Stefan Maxwell molecular diffusion coefficient</td>
<td>m$^2$.s$^{-1}$</td>
</tr>
<tr>
<td>$D'$</td>
<td>molecular diffusion coefficient in porous media</td>
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<tr>
<td>$D^\infty$</td>
<td>infinite dilution diffusion coefficient</td>
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<td>$D_{ij}^M$</td>
<td>Fickian molecular diffusion coefficient</td>
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</tr>
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<tr>
<td>$J^A$</td>
<td>total molar flux of component $i$ due to transport mechanism $A$</td>
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<td>Permeability</td>
<td>mD</td>
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<td>g.mol$^{-1}$</td>
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<td>$m$</td>
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<tr>
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<td>number of components in the mixture</td>
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<td>displacement of interface</td>
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<td>Definition</td>
<td>Unit</td>
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<td>$R$</td>
<td>radius</td>
<td>m</td>
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<td>separation of component $i$, defined as the difference between the mole fraction of $i$ at the top and bottom of reservoir</td>
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<tr>
<td>$T$</td>
<td>temperature</td>
<td>K</td>
</tr>
<tr>
<td>$t$</td>
<td>time</td>
<td>years</td>
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<td>$v_i$</td>
<td>molar volume of component $i$</td>
<td>m$^3$.mol$^{-1}$</td>
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<tr>
<td>$\mathbf{v}$</td>
<td>velocity vector</td>
<td>m.s$^{-1}$</td>
</tr>
<tr>
<td>$\omega$</td>
<td>rotational speed</td>
<td>rad.s$^{-1}$</td>
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<tr>
<td>$z$</td>
<td>vertical direction, positive upwards</td>
<td>m</td>
</tr>
<tr>
<td>$Z^{*}$</td>
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<td>$\varepsilon$</td>
<td>LJ potential depth</td>
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<td>$\Gamma$</td>
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<tr>
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<tr>
<td>$\delta_{ij}$</td>
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<td>$\rho$</td>
<td>mass density</td>
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<td>$\rho_{av}$</td>
<td>average mass density in the reservoir</td>
<td>kg.m$^{-3}$</td>
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<tr>
<td>$\sigma$</td>
<td>distance at LJ potential equal to zero</td>
<td>nm</td>
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<tr>
<td>$\tau$</td>
<td>tortuosity</td>
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<tr>
<td>$\phi$</td>
<td>porosity</td>
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**Subscripts**
- $e$: effective
- $f$: fluid
- $i$: component index
- $0$: reference condition

**Superscripts**
- $k$: time step
Acknowledgements

Firstly, I would like to thank God Almighty for his grace, his mercies and for making this possible. I would also like to offer my gratitude towards my PhD supervisors, Professor Ann Muggeridge, Professors Velisa Vesovic and Dr Nicolas Riesco for providing me with the opportunity to undertake this research. I would like to thank them for their guidance, critical feedback and their flexibility during my MSc and PhD programs.

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Abstract

The full understanding of the initial state of petroleum reservoirs and the fluxes that lead to compositional variations have become of huge interest to the petroleum industry. The compositional variation of reservoir fluid has great commercial impact on reservoir management and field development as it affects the value of the hydrocarbon in place, what recovery mechanisms applied and the treatment process of the extracted fluid if necessary.

Lateral and vertical variation in hydrocarbon density and composition between wells are observed in many oil reservoirs under appraisal. These gradations may be due to changes in reservoir filling over geological time, in which case the variations are not in an equilibrium state, or alternatively due to an equilibrium between chemical, thermal and gravity potentials. The mixing of non-equilibrium compositional distributions is affected by Darcy flows (if there is a resulting pressure gradient), gravitational overturning (if there is a density difference) and molecular diffusion. The diffusion flux may also be affected by gravitational and thermal effects. Previous work has focused primarily on convective mixing and simple models of mixing via molecular diffusion.

This work focuses on the rate of mixing via molecular diffusion, including the effects of pressure and thermal diffusion, which are modelled using the thermodynamics of irreversible processes for a single phase system. The interaction of diffusional mixing and gravitational overturning is also examined. The timescales to attain steady state are analyzed as well as the resulting compositional profiles. The developed model has been validated using simple transient analytical solution proposed by Carslaw and Jaeger (1959) for the molecular diffusion flux and Gardner et al. (1962) for the natural convection process. The diffusive fluxes in our model are also validated by steady state analytical solutions for species segregating in a thermo-gravitational column. The developed model was used to analyze the experimental results obtained for two ternary mixtures of methane, n-pentane and 1-methylnaphthalene; and methane, n-pentane and undecane by Ratulowski et al. (2003). Although 1-methylnaphthalene and undecane have similar molar masses, the system containing 1-methylnaphthalene resulted in a bigger grading (difference in mole fraction at the top and bottom of the system) than the latter. This analysis demonstrates the impact of real
mixture modelling (as opposed to the case when an ideal fluid is assumed) on the segregation-mixing process.

Finally, we show how the knowledge of the timescales for observed compositional variations to reach equilibrium can be used to estimate the time since a reservoir filled. The Madison formation in the LaBarge field in Wyoming, U.S.A was studied. This is an unusual gas reservoir, as non-hydrocarbons make up about 80% of the total gas composition, with methane constituting the remainder. The methane composition varies significantly, 22% at the crest of the formation to 5% near the GWC. There are several hypotheses in the literature behind the unusual gas composition and distribution in this formation (De Bruin, 2001; Stilwell, 1989; Huang et al., 2007). We use the fluid mixing model to test the various hypotheses. The results reveal that the geothermal gradient in this field is not sufficient to make the thermal diffusion and thermal convection process in this reservoir override the effect of the molecular diffusion. We conclude that the reservoir is not yet in compositional equilibrium as molecular diffusion will completely homogenize the composition variation in this field. We propose that the currently observe composition profile is as result of the formation being enriched with CO₂ at approximately 3 million years ago. This timescale is contemporaneous with the volcanic activity proposed by De Bruin (2001) and Stilwell (1989).
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Chapter 1

Introduction

1.1 Introduction

A full understanding of the fluxes that affect the composition distribution in the subsurface has a direct impact on the initial state of hydrocarbon reservoirs and the volume of the hydrocarbons in place. An accurate knowledge of the initial state of the petroleum reservoir is in turn very important as it is required to optimize reservoir management and field development. Observation of non-equilibrated fluid related properties in different parts of the reservoir, such as pressure gradients, contacts, fluid compositions and density could be indicative to the fact there are possible barriers to flow in the reservoir.

Field observations show a wide range of compositional variation; there is often a vertical compositional variation of components in reservoirs (Metcalf et al., 1988). In some reservoirs, horizontal compositional variations have also been observed. In yet others, the reservoir seems to have a uniform composition with respect to depth (Lee and Chaverra, 1998). In most reservoirs it is seen that the mole fractions of the lighter hydrocarbon decrease, where as the heavy fraction increases from the top to the bottom of the reservoir. However Temeng et al., (1998a), observed that in the Yufutsu field that the heavier components float above the lighter ones. These compositional variations can affect reservoir fluid properties (such as bubble point, dew point, and gas-oil ratio) considerably. The
difference in reservoir properties plays a key role in determining the reservoir primary drive mechanism and has a very huge impact on the selection of the recovery process.

Observation of non-equilibrium fluid properties within a reservoir may be evidence that a reservoir is compartmentalized. A failure to identify barriers in reservoirs significantly affects the development plan and could have a huge economic impact on the development plan. Conventional methods (3D seismic, position of fluid contacts, well logs, fluid pressure data and well test analysis) for the identification of compartments in reservoir usually identify the barriers or baffles to flow but do not give us any information on the strength of the barriers. This also usually requires the use of dynamic data (such as well testing) which require shutting down production of the wells and might be quite expensive (depending on the duration of the test). Studying the compositional variation (before production) provides a cheaper and early option (during the field appraisal) for the identification of the reservoir compartmentalization. This will help plan optimum extraction programs.

The tools required to fingerprint oil composition and to measure other fluid properties variation (such as pressure gradients, density and fluid contacts) during the appraisal of the field are readily available. Examples of these tools include: drill-stem test (DST) samples, repeat formation test (RFT) and MDT are carried out at various locations in the field. Studying the timescales involved for this measured fluid variations to reach equilibrium since the time the reservoir was charged, we can infer whether the reservoir is compartmentalized. Using this tool, we can also obtain properties of the barriers (example the transmissibility of the fault) that will be required to produce the non-uniform fluid property in the reservoir (England et al., 1995).

The spatial distribution of fluid components in reservoirs is usually a product of the reservoir filling process (progressive source-rock maturation and hydrocarbon migration). During petroleum filling, a source rock that is progressively being heated expels oils with gradually changing composition, and so with time the GOR increases. The part of the reservoir with furthest away from the kitchen receives the lightest fluids while the heavier fluids (least mature) are contained in the part closest to the source rocks. In some cases, more than one source rock kitchen charges oil to the field. These kitchens may have different compositions or temperatures, thus leading to an oil distribution between different parts of the reservoir. Other process such as: fluid migration, leaky seals, chemical reactions, gravity,
Biodegradation and asphaltene precipitation (Høier and Whitson, 2000) are also believed to alter compositional variation in hydrocarbon fields.

There are four main mechanisms that modify compositional variation after reservoir filling before production (that can be described using the thermodynamics of irreversible processes): 1) pressure diffusion 2) thermal diffusion, 3) molecular diffusion, and 4) natural convection. Natural convection is the bulk movement of fluid due to density gradients. These density gradients are established by concentration and/or geothermal gradients. Natural convection due to concentration gradients is referred to as gravitational overturning, while convection due to thermal gradients is referred to as thermal convection. Molecular, pressure and thermal diffusion are molecular fluxes that arise due to composition, pressure and thermal gradients, respectively. The magnitude of these diffusion fluxes is dependent on the product of the respective diffusion coefficient and driving forces (gradients). While thermal and pressure diffusion tend to cause segregation of fluid components in the subsurface, thermal convection and molecular diffusion on the other hand tend to homogenize the compositional variation.

Figure 1-1: The effects of various mass transfer mechanisms on the composition in a simple 3D reservoir (England et al., 1987).
Figure 1-1 illustrates the impact of molecular diffusion and convection on the lateral and vertical fluid composition gradients. Fig. 1-1(a) shows the compositional variation inherited from reservoir filling. Molecular diffusion (alongside pressure diffusion) will rapidly cause vertical thermodynamic equilibrium within the individual wells on a geological timescale. Hydrocarbon reservoirs usually have a larger lateral distance compared to their thickness, therefore it will take longer for lateral equilibrium to be attain. Thus Figure 1-1 (b) shows that wells 1, 2 and 3 have different average compositions. Given sufficient time for diffusion to occur, the composition of the different wells would eventually approach each other, but the gravitational induced compositional gradient will exist. This can be observed in Fig.1-1 (c). If however, thermal convection occurs, the entire reservoir will become homogenized (Fig. 1-1 (d)). The reader should note that the impact of thermal diffusion has been neglected in this example. This phenomenon can either enhance or weaken the equilibrium concentration gradient, depending on the magnitude of this flux.

Compositional variation modelling integrates the various concepts described in the previous paragraphs. It involves the modelling of the convection and diffusion process and the impact these fluxes have on equilibrium composition and times. If we have only a few fluid compositions from appraisal wells, we can use modelling to predict the compositions at the other positions in the reservoir. This is a key part in the process of building a good reservoir model as this will provide a better idea of the initial state of the reservoir prior to production. Thus defining important initial reservoir characteristics such as density stratifications in the reservoir; and initial fluid in place. Another application of compositional variation modelling is the early identification of reservoir compartmentalization. Studying the timescales necessary for the fluid composition to reach equilibrium (once the processes causing the initial fluid variation have stopped) under the influence of the convection and diffusion processes and comparing this to the reservoir age or the likely time since any fluid perturbation processes ceased can be used to determine if the fluid variations reflect compartmentalization or simply incomplete mixing. This is the main aim of this thesis.
1.2 Literature Review

In the last two decades, there have been several attempts to study and model the fluxes responsible for compositional variation in hydrocarbon reservoirs. Initial studies on this topic consider only the effect of gravity on compositional variation in one dimensional (1D) convection-free systems (Sage and Lacey, 1939, Schulte, 1980, Montel and Gouel, 1985, Wheaton, 1991). The general conclusion of these studies is one that is well established; they show that gravity causes the heavier components to segregate towards the bottom of the reservoir. Thermal diffusion in a 1D convection-free system was accounted for in both binary and multi-component mixtures by (Holt et al., 1983, Whitson and Belery, 1994). From these studies it was concluded that thermal diffusion can have the same order of magnitude and may have the opposite effect of gravity (pressure diffusion). Thus, this flux might improve or reduce the segregation caused by gravity, depending on the sign convention of the thermal diffusion coefficient.

The concept of molecular diffusion is described extensively by Taylor and Krishna (1993). This phenomenon usually leads to a uniform mixture in hydrocarbon reservoirs when fluid are modelled as ideal (England et al. 1987). Belery and Da Silva (1990) investigated the impact of molecular, pressure and thermal diffusion in the Ekofisk field (using a convection-free one dimensional (1D) model). Their model was based on effective molecular diffusion coefficients and effective thermal diffusion factors. The results obtained from this study show some qualitative agreements with the components distribution observed in the field.

Ghorayeb et al., (2003b) developed a theoretical convection-free diffusion model based on irreversible thermodynamics to reproduce the unusual compositional variation observed in the Yufutsu field. Their results show that thermal diffusion causes the heavier components to segregate to the top of the reservoir, overriding the gravity effect. They conclude that thermal diffusion is the main phenomenon affecting the density and species distribution in the reservoir. More recently, Joseph and Imo-Jack (2013) used diffusion modelling to predict whether a significant oil-rim was present in the Niger Delta fields. They used this tool along with flash calculations to locate whether gas-oil contact existed in the field. Their model gave acceptable results when uncontaminated PVT fluid samples were available and where the fluid column was continuous (no barriers to flow).
Galliero and Montel (2008 and 2009) studied the compositional grading in (convection-free) petroleum reservoirs using molecular dynamics simulations. In these works, thermodynamic modelling based on equation of state (EOS) and molecular dynamics (MD) simulations were applied for the calculation of the fluid distribution in a 2D domain. MD results provided insights on the time evolution of the fluid distribution and the calculated profile was used to tune the EOS model. The results obtained were found to be consistent with profiles obtained from an analytic solution (for systems for which this exists). The MD simulations also confirmed the non negligible impact of thermal diffusion on the concentration profiles for the fluid sample studied. All the above studies assume a convection-free system; neglecting the effect of convection on the compositional variation although it may be very important in some reservoirs. These studies were also carried out in 1D vertical system; thus lateral compositional variations were not investigated.

The combined effect of convection and diffusion has been investigated by several authors. However, the majority of these researchers assume that the onset of convection is due to vertical geothermal gradients high enough to generate instabilities that induce thermal convection (Bedrikovetskii et al., 1993). However, the possibility of this type of convection is negligible in hydrocarbon reservoirs (Horstad et al., 1990), who showed that for typical reservoir properties the critical Rayleigh number will only be exceeded if abnormally high geothermal gradients existed in the reservoir. They also investigated the reason behind the variation in the fluid composition in the Gullfaks field, located in the Norwegian North Sea. They found that the observed petroleum compositional heterogeneity was consistent with diffusion being the dominant mixing process. The combined effect of natural convection (due to horizontal temperature gradients) and diffusion on compositional variation in hydrocarbon reservoirs has been studied by Jacqmin (1986, 1990) and Moser (1986). Jacqmin’s work shows the mixing effect of convection. He observed that the stronger the convection the more uniform the composition. However, these authors neglected the effect of thermal diffusion.

Riley and Firoozabadi (1998) have also studied the impact of convection and diffusion on species distribution in the subsurface. This work investigated the impact of these fluxes on a binary single phase fluid with a prescribed linear temperature field in 2D. This study shows that a small amount of convection can lead to an increased horizontal compositional gradient. Ghorayeb and Firoozabadi (2000a) modelled the impact of diffusion and convection on
multi-component hydrocarbon mixtures in a 2D porous media using a finite volume method. They showed the importance of considering the competing diffusion mechanisms in a multi-component fluid, as methane segregates to a different part of the field when only a binary mixture is considered. They also demonstrated that depending on the fluid mixture, weak convection may drastically change the steady state compositional variation.

Nasrabadi et al., (2006) modelled the impact of diffusion and natural convection (due to horizontal geothermal gradients) for a two-phase multi-component system in 2D. They computed the location of the gas-oil contact and species distribution in two-phase reservoirs based on a given pressure and composition at a reference point in a reservoir with known permeability and temperature profiles. Their model was extended to calculate the initial state of two-phase reservoirs using available well data. Their results highlight the importance of natural convection on the GOC. They show that the initial slightly slanted GOC in a convection-free system becomes horizontal at steady state due to the implementation of convection (gravitational overturning). They also found that thermal diffusion had the opposite effect to gravity and decreases the segregation in the systems studied.

More recently, Besong (2010) modelled the impact of gravity and molecular diffusion in a 1D single phase multi-component system. This paper modelled these phenomena using the thermodynamics of irreversible processes. Using the latest developments in this field, this work was able to explain the abnormal segregation observed in Ratulowski’s et al., (2003) experiment. In their experiments, they observed that the methane separation was greater in a ternary mixture of methane, n-pentane and methylnaphthalene compared to the mixture of methane, n-pentane and n-undecane, even though the two mixtures only differ by their last component, which have similar molecular weights. Besong (2010) also carried out sensitivity analysis on all the parameters that affect the molecular and pressure diffusion fluxes. It was found that the impact of excess molar volumes on the segregation-mixing process is negligible. The model used by Besong (2010) will form the basis of the model developed in Chapter 3 in this thesis.

Conventionally, reservoir compartmentalization is inferred when fluid properties such as pressure gradients, fluid density, and composition and fluid contacts are not in equilibrium and not similar in different parts of the field. The idea behind this is that over a period of time (based on geological timescales) the fluid properties should have reached equilibrium and
thus should be the same throughout a continuous reservoir, except if barriers to flow are present. This concept alongside conventional reservoir appraisal techniques can be used as a probabilistic tool to infer whether the reservoir is connected. Examples of these exploration tests include; repeated formation tests (RFT), seismic, wire line logs, drill stem test and modular formation test (MDT). However, these tests carried out during appraisal have their setbacks especially that of the distance of the investigation carried out. For example gamma ray and resistivity logs may correlate a shale layer across several appraisal wells. However, this shale layer may not be laterally extensive throughout the field. The seismic mapping tool has been employed by geophysicists to identify faults in the reservoir. However, some faults are sub-seismic and will not show up on seismic map as they do not have big enough fault heave (Davies, 2004). These sub seismic faults are generally small faults; however large amounts of them can greatly impede flow. Seismic data also does not provide any direct information of the transmissibility of the fault.

Dynamic data obtained from well testing can also be used to check whether the barriers are present in the reservoir and obtained certain characteristics of the barrier such as fault length and position of the boundaries. This technique is however plagued with the fact that the results obtained may differ due to the duration of the tests and the position of the test wells. The cost of the well test which increases with the duration, results in most operators performing shorter test which may not be enough to ‘see’ the barrier (Smalley and Muggeridge, 2010).

Observation of non-equilibrium fluid properties in the subsurface is not a definite sign of reservoir compartmentalization. Hydrocarbon reservoirs are subjected to various processes that could lead to heterogeneous fluid properties. For example on-going (Matava et al., 2003) reservoir filling will result in varying density and composition across the field either laterally or vertically. This would also affect the position of the fluid contacts. Biodegradation in the reservoir will have similar effects (Smalley and Muggeridge, 2010). Also, reservoir fluid properties may be not be in a state of equilibrium because there has not been sufficient time for the system to mix (or reach equilibrium) since the reservoir was perturbed (this is usually since the time when the reservoir was filled).
The concept of reservoir compartmentalization has been touched on by several authors. Smalley et al. (2004) and Smalley and Muggeridge (2010) highlight the benefits of using the knowledge of timescales of fluid mixing mechanisms to infer compartmentalization in oil and gas reservoirs. Comparison of the time it would take for a fluid difference to mix with the actual time available for mixing to occur allows one to find out if there are barriers to fluid communication and to estimate the degree of compartmentalization. These papers used existing order of magnitude equations to estimate the mixing times for the four main types of variation in fluid properties (fluid pressure, fluid contacts, fluid density and fluid chemistry). The mixing times for the different fluid mixing processes were compared by applying the equations to a range of simple fluid scenarios in one simple reservoir description. This study shows that mixing times for fluid mixing processes are diffusion > fluid density (gravity overturning) > fluid contacts > fluid pressure.

Smalley and Muggeridge (2010) highlight how reservoir compartmentalization affects oil recovery. In their work, they state that the drainage efficiency (related to the portion of the field connected to the producing well) and the sweep efficiency (representing the degree to which oil is swept from the drained volume into the producing well) are mainly affected by compartmentalization (Fig.1-2). They analyzed the effect of compartmentalization on these two parameters. It was stated that it is more difficult to mitigate the effects of barriers and baffles on sweep than on drainage (poor drainage can be fixed by subsequent field activity such as drilling more wells).

England et al., (1995) studied the impact of compartmentalization on the density-driven convection process. This work used Schlumberger’s ECLIPSE black oil simulator to model the gravity overturning process (density driven natural convection) in a reservoir with a barrier to produce the present-day density variation observed in the Forties field. The simulation results show that the only a model with a 1% transmissibility barrier between the main and SE part of the reservoir could possibly result in the fluid density variation observed in the field.
Figure 1-2: Figure illustrating how hydrocarbon recovery is affected by compartments in reservoirs (Smalley and Muggeridge, 2010).
Go et al., (2012) used data from appraisal wells and the reservoir mixing timescales alongside with interpretations from logs and seismic data to investigate the vertical and horizontal compartmentalization in the Horn Mountain field (Gulf of Mexico). They used order of magnitude estimates for the timescales to also quantify the properties of the barriers to flow identified. They confirmed that the faults previously found from seismic data were indeed barriers to flow. They also suggested that the lateral pressure and density changes were due to reservoir compartmentalization in this field; however the lateral compositional variations were not, as the timescales for mixing by molecular diffusion is larger than the time since the reservoir was charged.

It has been illustrated in the previous paragraphs that that the impact of diffusion (molecular, pressure and thermal) and convection on composition variation in hydrocarbon reservoirs has been studied extensively in previous years. Most of these studies are focused on the impact the fluxes have on the equilibrium or observed compositional profile. In our work, we are not only interested in this, we also interested in the timescales it takes for the processes to reach steady state. The effect of compartmentalization has been studied using order of magnitude equations to calculate the timescales of the fluid mixing processes. Compositional heterogeneity caused by compartmentalization has been, however, studied on a bulk fluid scale as explained in the previous paragraph. Previous works have not studied compartmentalization which incorporates extensive modelling of the main segregation-mixing processes (diffusion and convection). In this work, we shall integrate both concepts, and use the timescales for thermodynamic equilibrium to compute the time since the hydrocarbon reservoir was charged with the fluids.

1.3 Thesis Aims and Objectives

In this thesis, we will integrate the concept of modelling the fluid variation caused by diffusion and natural convection with that of reservoir compartmentalization. We shall use the timescales of the fluxes that lead to fluid mixing to determine when the reservoir was charged with its fluid and the composition of the source fluids. We aim to model the multi-component convection and diffusion process in a porous media using the theory of the thermodynamics of irreversible processes to calculate the timescales for equilibrium for these
processes. If this timescale is small compared to the time elapsed since the variation in composition arose (since reservoir filling), we infer that the reservoir is compartmentalized.

The main objectives of this thesis are listed below:

- To carry out an extensive study of the impact the diffusion and convection fluxes would have on steady state composition and timescales using a 2D numerical model based on thermodynamics of irreversible processes.
- To use these tools to study the sensitivity of the timescales and steady state composition to typical reservoir characteristics such as; reservoir inclination, initial composition and density variation, thermal gradients and heterogeneity (stochastic shales and permeability layering).

1.4 Case Studies

In the thesis we use the compositional modelling as a tool to interpret the unusual gradients that exists in the Madison reservoir in the LaBarge field in Wyoming, U.S.A. The gas composition of this reservoir varies significantly throughout the reservoir averaging 66% CO₂, 21% methane, 7% H₂S and 1% He. Previous work on this field (Huang et al., 2007 and confidential work by BP) has tried to reproduce this profile. The first study by ExxonMobil (Huang et al., 2007) suggests that fluid mixing by molecular diffusion after 50 million years reproduces the current methane profile. However this study does not describe the methods or disclose parameters used as this was not the main task of their work. Discussions with Hongjun Lou from BP about the latter mentioned in-house study form the hypothesis for this study. We thus investigate the impact the convection and diffusion fluxes have on the composition profile in this reservoir and use the timescales needed to reproduce the observed LaBarge profile to constrain how long ago the reservoir was filled. We obtain a rather different conclusion from these two initial studies.

We will also use this tool in this work to reproduce results obtained from the experiments carried out by Ratulowski et al., (2003). In their work, they noticed an unexpected difference in the degree of separation when they carried out centrifuge experiments in methane/n-pentane/n-undecane and methane/n-pentane/methylnaphthalene (MNP) mixtures. The two
mixtures only differ in the last components, both of which similar molecular weights. However, the methane mole fraction separation in the former mixture is a factor of eight less than in the latter mixture of equivalent composition. As part of this work, we provide a justification of this difference.

1.5 Thesis Outline

In Chapter 1, we introduced the subject matter which forms the background for this thesis. We also perform an in depth literature review into the subject matter. Relevant previous works on the dynamics of the convection and diffusive fluxes and how they affect compositional grading in porous media are reviewed. The major findings of these works are highlighted and we give reasons why this work is complementary to previous works. In Chapter 2 we describe the main fluxes that will be studied in this work and other factors that affect them such as non-ideality of the fluid and the diffusion coefficients. We also shed some light on a related topic of the instabilities that may arise due to convection.

We develop a one dimension mathematical model for diffusion processes (molecular, pressure and thermal), in Chapter 3. The aim of this work is to investigate the impact of the diffusion fluxes on the steady state composition and timescales for equilibrium. We also propose a new analytical solution to predict the steady state composition for an ideal multi-component mixture under the influence of just pressure and molecular diffusion. Our new model outperforms the previous model, as does not require prior knowledge of the steady state mole-fraction at a reference point. In the final section of this chapter, we reproduce the segregation observed in the centrifuge experiments performed by Ratulowski et al., (2003) and investigate the impact of reverse diffusion on the ternary mixtures studied.

In Chapter 4, we perform a study on the impact of natural convection and molecular diffusion in a two-dimensional reservoir. We carry out sensitivities studies on different parameters (reservoir tilting, heterogeneity, thermal gradients and initial graduated compositional variation) which represent different scenarios that are usually present in hydrocarbon reservoirs and we present the effects on the equilibrium time and composition.

We study a field example in Chapter 5. We show how the individual fluxes (both convective and diffusive) affect the steady state composition and times of the mixture in the Madison
reservoir in the LaBarge field. The aim of this exercise is to compare the steady state and transient compositions obtained from our tool to that presently observed in the field. This helps us to infer whether the field is at steady state and the time the reservoir was charged with the fluids.

Chapter 6 concludes this thesis with the summary of our key findings and we highlight the future areas of research that must be explored.

A list of references cited in the text is found at the end of the thesis. In the Appendices, we include the algorithm for the 1D diffusion numerical code (A.1) and the extensive derivation for the analytical solution (A.2). We also show the correlation we used to calculate the molecular diffusion coefficients used in this work and how the data needed for their calculations were obtained (A.3). In Appendix A.4, the Stefan-Maxwell formulation for multi component systems is elaborated.
Chapter 2

Theoretical Background

Variations in hydrocarbon density and composition between appraisal wells are observed in many hydrocarbon reservoirs during the exploration stage of field development (Temeng et al., 1998; Ghorayeb et al., 2003; Metcalfe et al., 1988 and Hamoodi et al., 1996). For this reason, there has been an increasing interest in the petroleum industry to have a full understanding of the fluxes that affect the composition distribution in the subsurface as this has a direct impact on the initial state of hydrocarbon reservoirs. This compositional variation can also be used to infer the time since which the reservoir was charged with its fluid or bound the reservoir’s connectivity. The aim of this work, as described in the previous chapter, is to study the effect convection and diffusion has on compositional variation in hydrocarbon reservoirs after the filling process. In this chapter, we shall discuss the reservoir filling process and the various physical mechanisms (fluxes) that shape out the compositional variation in a hydrocarbon reservoir.

2.1 Fluid Entrapment and Filling

It is generally accepted that petroleum is formed in the subsurface in fine grained source rock. Some fraction of the organic remains of dead organisms deposited with the rocks may be preserved to form kerogen. Kerogen is broken down to produce mobile petroleum fluid at temperatures of about 100°C. If the volume of petroleum within the pores is adequate to form
an inter-connected phase, expulsion may occur (Cooles et al., 1985). Marine source rocks tend to be oil-prone, whereas terrestrial source rocks tend to be gas-prone (Schlumberger Oilfield Glossary, 1998). In the source rock, as temperature increases the gas to oil ratio (GOR) increases. This is because the less stable high molecular weight components become cracked to more stable lighter components. As the source rock matures, less dense oil with increasing GOR and API density is produced.

To create accumulations from which petroleum can be extracted economically, the generated petroleum must migrate from the low permeability source rock into the pores of coarser, more permeable ‘reservoir’ rocks and be sealed off by trap (a fine-grained cap-rock). The distance involved in this process is usually up to 100 km, but depends on the volumes and types of petroleum and rocks involved. The main driving force for the migration of petroleum fluid is buoyancy (Schowalter, 1979). The magnitude of the buoyant force is governed by the density difference and the height of the petroleum column. Capillary pressure on the other hand is the main resisting force to primary migration. The expelled oil has to displace water originally in the pores of reservoir rock, to form a petroleum accumulation that is economically viable. Previous work by England et al., (1987) suggests that fluid released from the fine-grained source rocks, migrate vertically (up or down) into layers with higher permeability. The petroleum fluids will remain in these permeable layers until they overcome the capillary pressure in the layers surrounding them. When this occurs, the fluid will move vertically until another lateral highly permeable layer is reached. This would lead to a dendritic network of petroleum from the source rock (Fig. 2-1(a)). The migrating fluids will flow through layers with larger pores. The petroleum advances into the trap via series of fronts that reflect the changing composition of the petroleum fluids leaving the source rocks (Fig. 2-1(b)). As the expulsion of petroleum is prevented by the overlying seal, fresh petroleum from the source rock is forced to travel through smaller pores (Fig 2-1(c) and 2.1(d)). This leads to a more continuous petroleum accumulation. As more petroleum is charged into the trap, the buoyancy forces will increase with the increasing height of the connected petroleum accumulation. This would help overcome the larger capillary pressures present in the smaller pores; thus displacing the water in them. This process will continue until the petroleum column has enough buoyancy pressure at its crest to overcome the capillary pressure acting between the reservoir and the overlying cap rock.
After the migration of the petroleum fluid into the trap, several fluxes (such as: leaky seals and biodegradation to name a few) may enhance the compositional variation; while diffusion and convection tend to homogenize the composition distribution of the hydrocarbons in the subsurface. Given enough time, the distribution of the petroleum fluid in the subsurface will attain steady state. Thermodynamically, steady state composition distribution is governed by diffusion and natural convection. Compartmentalization on the other hand might hamper the attainment of steady state in the whole reservoir. In the next section, we shall introduce each of the phenomena that influence the reservoir fluid composition.

![Figure 2-1: The proposed mechanism for reservoir filling (England, 1989).](image)

### 2.2 Diffusion

The diffusive fluxes that affect the species distribution in subsurface are: (1) molecular diffusion, (2) pressure diffusion (gravity diffusion in a hydrostatic system), and (3) thermal diffusion. The timescales for these fluxes are governed primarily by the diffusion coefficient.
of each component in the mixture, tortuosity, the compositional or thermal gradient (the magnitude of the driving forces) and the size of the reservoir.

### 2.2.1 Molecular Diffusion

Molecular diffusion describes the passive movement of molecules, due to random motion (Brownian motion). This process tends to reduce and eventually eliminate chemical potential gradients (which are equivalent to compositional gradients) by the random motion of molecular species. Diffusion will cause the redistribution of matter so that any horizontal concentration gradients will be eliminated and vertical gravitational or thermal induced compositional gradients become established. The molecular diffusion species equation for a multi-component multi-phase mixture is given below:

\[
\frac{\partial}{\partial t} \left( \sum_{k=1}^{n_c} S_k c_k x_{ik} \right) = \nabla \left( \sum_{k=1}^{n_c} \left( S_k c_k \sum_{j=1}^{n-1} D_{kij}^M \nabla x_{kj} \right) \right) \quad i = 1, ..., n - 1 \tag{2-1}
\]

where \( c_k \) is the concentration of the mixture in phase \( k \), \( x_{ki} \) is the mole-fraction of component \( i \) in phase \( k \), \( S_k \) is the saturation of phase \( k \) and \( D_{kij}^M \) is the Fickian diffusion coefficient of \( i \) in \( j \) in phase \( k \). In this work, we only deal with single phase mixture, thus the diffusion equation is:

\[
\frac{\partial (\phi c x_i)}{\partial t} = \nabla \left( c \sum_{j=1}^{n-1} D_{ij}^M \nabla x_j \right) \quad i = 1, ..., n - 1, \tag{2-2}
\]

We include the porosity term on the left hand side of Eq. 2-2 to take into account diffusion in porous medium. Taylor and Krishna (1993) present a general derivation of the molecular diffusion flux for multi-component mixtures. In this case, Eq. 2-2 can be expressed as a vector equation, and the diffusion coefficients \( D_{ij}^M \) are represented as elements of a matrix.

The reader should note that in Eq.2-2 and subsequent diffusive flux equations that we have assumed that the variation in the overall composition in the system is negligible compared to the variation in composition, hence the overall concentration can be assumed to be constant. This is because in the systems dealt with in this work, changes in composition, temperature and pressure are small enough, thus the molar density can be approximated as a constant. To model molecular diffusion problem we need the diffusion coefficients. This parameter mainly
affects the timescales for the mixing process. To obtain near accurate timescales we need to use appropriate molecular diffusion coefficient values. There is a vast body of literature on molecular diffusion coefficients of binary systems (Cussler, 1976). A sizable amount of binary data on hydrocarbons is also available (Dysthe and Hafskjold, 1995, Sigmund, 1976). However, molecular diffusion coefficients for mixtures containing three or more components, especially for hydrocarbon mixtures at reservoir conditions are scarce. Thus, we need a correlation to predict the diffusion coefficients of hydrocarbon systems at these conditions. In this work we adopt the correlation presented by Leahy-Dios and Firoozabadi (2007) and Kooijman and Taylor’s correlation (1991) to calculate the molecular diffusion coefficients. These authors reviewed several models for predicting molecular diffusion coefficients in multi-component mixtures and compared them with their correlation; it was concluded that their correlation provides the best results compared to the other models.

2.2.2 Pressure Diffusion

Pressure diffusion is driven by pressure gradients that occur in the reservoir. Bird et al., (2002) and Firoozabadi (1999) present the derivation of the pressure diffusion equation based on the thermodynamics of irreversible processes. This phenomenon is also referred to as gravity diffusion or gravity segregation if the system has hydrostatic pressure. Using the thermodynamics of irreversible processes, the pressure diffusion species equation for a multi-component mixture with hydrostatic pressure is given by:

$$\frac{\partial (\phi c x_i)}{\partial t} = -\nabla \left\{ c \sum_{i=1}^{n-1} D_{ij} \frac{g}{RT} x_i \left( \frac{\bar{v}_i}{M_i} - \frac{1}{\rho} \right) \nabla P \right\}, \quad i = 1, ..., n - 1, \quad (2.3)$$

where $\rho$ is the mass density of the mixture, $R$ is the ideal gas constant, $T$ is the temperature, $M_i$ is the molar mass of component $i$, and $g$ is the acceleration due to gravity. In this work, we model reservoirs in which the only pressure gradient is due to gravity. Due to the considerable heights of hydrocarbon columns, gravity diffusion tends to alter the equilibrium concentration; so they vary with depth. This results in the denser components segregating to the bottom of the reservoir, and lighter components to the top.
2.2.3 Thermal Diffusion

Thermal diffusion is not only important for the study of compositional variation in the subsurface (Whitson and Belery, 1994; and Ghorayeb and Firoozabadi, 2000b), it is also important for the separation of isotopic mixtures (Rabinovich et al., 1979; and Galliero and Montel, 2008 and 2009) among other uses. Thermal diffusion (also known as the Soret effect) is the tendency for a convection-free mixture to separate under the influence of a temperature gradient. The thermal diffusion coefficient $\alpha$, is a measure of the thermal diffusion process, and its sign convention determines the direction of this process. Calculations based irreversible thermodynamics indicate that thermal diffusion may have the same order of magnitude as pressure diffusion. This process may thus enhance or weaken the segregation process in mixtures. Using thermodynamics of irreversible processes, the equation for the movement of species due to thermal diffusion flux is given by:

$$\frac{\partial (\phi c x_i)}{\partial t} = \nabla \left\{ c \sum_{i=1}^{n-1} D_{ij}^M \kappa_{T_i} \nabla \ln T \right\}, i = 1, ..., n - 1,$$

where $\kappa_{T_i}$ is the thermal diffusion ratio of each species $i$ and is defined by:

$$\alpha_i = \frac{\kappa_{T_i}}{x_i x_n}$$

and $\alpha_i$ is the thermal diffusion coefficient.

There has been confusion in literature in representing the direction of $\alpha_i$ either in experiment or theory. For example, the experimental data of Rutherford and Roof (1959), for a binary mixture of methane and n-butane, show that the component $i$ segregates to the hot region when $\alpha_i > 0$, and to the cold region when $\alpha_i < 0$. In contrast, in the theoretical models of Kempers (1989) and Rutherford (1963), positive values of the thermal diffusion coefficient lead to the component going to the cold part of the reservoir. In this work, a positive thermal diffusion ratio will indicate the migration to the hot region in the reservoir. This is normally the bottom as the geothermal gradient is such that temperature increases with depth.

The magnitude of the geothermal gradient depends on the thermal conductivity of the rock and heat flux. Sometimes the thermal conductivity of the reservoir rock is not uniform; this is due to mineralogical composition of the rocks, porosity and presence of gas or water. These
different thermal conductivities will result in an inhomogeneous temperature gradient. This inhomogeneous temperature gradient may cause thermal diffusion leading to unusual species distributions.

Previous work indicated that thermal diffusion coefficients are sensitive to intermolecular interactions and the size and shape of molecules. Their magnitudes are also governed by thermodynamic conditions (Kincaid et al., 1987). In many mixtures, due to the small magnitude of the thermal diffusion coefficient and/or the obscuring effect of thermal convection, accurate thermal diffusion coefficient measurements are difficult to perform experimentally. Experiments in micro-gravity have been proposed to deal with this difficulty (Georis et al., 1998). Consequently, accurate data of $\alpha$ are sparse. Vargaftik (1975), Tyrell and Harris (1984), Ma et al., (1983) and Köhler and Muller (1995) have presented detailed descriptions of the different techniques for measuring thermal diffusion coefficients. The oldest method reported involves using a thermo-gravitational column technique. The technique was originally used to obtain thermal diffusion coefficients for binary mixtures. This technique has been extended for multicomponent mixtures (Marcoux et al., 1999; Haugen and Firoozabadi, 2005; Leahy-Dios and Firoozabadi, 2005). This method is slow, has limited accuracy and requires samples to be removed from the test mixture for analysis. Sampling disturbs the diffusion process and terminates the experiments, thus all measurements come from separate experiments. Another technique used which provides faster and more accurate measurements is the optical method. It uses laser beams passing through the test mixture to obtain the coefficient. The higher accuracy of this technique is a result of the fact that sampling is not required and transient measurements can be made. A number of authors have used this technique to determine both thermal and molecular diffusion coefficients for several binary mixtures (Meyerhoff and Nachtigall, 1959; Giglio and Vendramini, 1975 and 1977; and Zhang et al., (1996)). More recently, Haugen and Firoozabadi (2006) satisfactorily extended this method for multicomponent mixtures.

Several theoretical approaches have been suggested in the literature to describe thermal diffusion factors with varying success (Rutherford, 1963 and Kempers 1989). These models were able to describe the thermal diffusion factors in some binary mixtures qualitatively. However the work by Shukla and Firoozabadi, (1998) Firoozabadi et al., (2000) made a significant improvement in the prediction of this property as their method incorporated both
the equilibrium and non-equilibrium properties of mixtures (previous models only incorporated equilibrium properties). Their model out performed previous models when tested for both hydrocarbon and non-hydrocarbon mixtures; however all models failed to provide accurate results near the critical point.

The behaviour of thermal diffusion coefficients for mixtures near the critical region has been well documented in literature (Anisimov and Kiselev (1992), Anisimov et al., (1995), Cheng et al., (1997) Rutherford and Roof (1959) to name a few). Firoozbabdi (1999) point out that in low pressure gas mixtures and ideal liquid mixtures $\alpha$ is small but that it is large in non-ideal liquid mixtures. This parameter becomes very large in the near-critical region for both liquid and gaseous mixtures. In this respect, $\alpha$ and the molecular diffusion coefficient have opposite trends. The molecular diffusion coefficient is big for low pressure gas mixtures and become small as the critical region is reached.

Thermal diffusion coefficients in multi-component non-ideal mixtures may differ from those in binary mixtures (Leahy-Dios et al., 2005). Sakonidou et al., (1998) and Rutherford and Roof, (1959) investigated binary mixtures containing methane. In their work methane segregates to the hot region. In contrast, in the work of Belery and da Silva, 1990 and Temeng et al., 1998, where they study multicomponent mixtures containing methane, the methane segregates to the cold region.

2.2.4 Diffusion in Porous Media

The equations presented so far for the diffusion process have been derived for mixing in a free space. Reservoirs are formed of porous rocks and diffusion is reduced as molecules cannot travel freely; rock grains obstruct their path. To include the effect of porous media on molecular diffusion coefficients we use the formula proposed by Brigham et al., 1961 and Perkins and Johnston, 1963.

\[ D' = \frac{D}{F\phi} \tag{2-6} \]

where $D'$, $D$ and $F$ are molecular diffusion in porous media, molecular diffusion in free space and the formation resistivity factor, respectively. The formation resistivity factor can be found from Archie’s first law (Archie, 1942):
In this equation, $a$ represents the tortuosity factor and $m$ is the cementation factor. The term $\frac{1}{F_\phi}$ usually varies between 0.15 and 0.7, depending on the lithology (Brigham et al., 1961). It can be seen immediately that the mixing process by diffusion and the subsequent mixing timescales will be significantly reduced in the porous medium compared with the bulk fluid. Taking a cementation $m$ to be 2 and a porosity to be 0.2 reduces the diffusion coefficient by a factor of 0.2. This will be reduced further if the rock is partially saturated with water. There is little work on the impact of porous media on thermal and pressure diffusion coefficients. However, a porous medium is expected to affect these phenomena in a similar way. In this work, we plan to use a similar technique as Eq. 2-7 to model the effect of porous media on thermal and pressure diffusion.

### 2.2.5 Non-Ideality

As opposed to real mixtures, ideal mixtures are ones which do not have any excess thermodynamic quantities. Molar volumes and molar free energy are some examples of these quantities. In an ideal mixture, there is no change in volume when two or more substances dissolve to form a mixture. Thus, the molar volume of the mixture is the weighted average of the molar volume of its constituents. Ideal mixtures are hypothetical models which are used for simplicity when deemed a good approximation for real mixtures.

A real mixture under the influence of molecular diffusion and thermo-gravity segregation differs quantitatively from an ideal one by the presence of excess molar volumes and/or gradients of the natural logarithms of the activity coefficient. The former accounts for the non-ideality in the pressure diffusion process, while the latter represents this in molecular and thermal diffusion. Besong (2010) found that the excess molar volumes had negligible effects on the gravity segregation process, thus it is safe to assume that for a given species $i$ the partial molar volume is equal to the molar volume ($\bar{v}_i = v_i$). In this work, we therefore only investigate the impact of the thermodynamic factor when modelling the diffusion process for real mixtures. Taylor and Krishna (1993), described the driving force for non-ideal fluids using:
where $\mu_i$ is the chemical potential. The subscripts in the gradients terms signify that the derivation is calculated by keeping the composition of species $i$ constant. This is computed at constant temperature and pressure. Substituting $\mu_i = RT \ln \gamma_i x_i$, we obtain the expression for the driving force for diffusion in terms of the thermodynamic factor, $\Gamma$ and the compositional gradient:

$$d_i = \frac{x_i}{RT} \nabla_{T,P} \mu_i = \frac{x_i}{RT} \sum_{j=1}^{n-1} \frac{\partial \mu_i}{\partial x_j} \nabla x_j$$  \hspace{1cm} 2-8

The thermodynamic factor can be defined as function of the gradients of the natural logarithms of the activity coefficients (or fugacity coefficients when dealing with non-ideal dense gas mixtures) with respect to the mole-fractions:

$$\Gamma_{ij} = \delta_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,P,S}$$  \hspace{1cm} 2-9

where $\gamma_i$ is the activity coefficient of component $i$ and $\delta_{ij}$ is the Dirac delta function ($\delta_{ij} = 1$ if $i = j$ and equals zero otherwise). In this work, the fugacity coefficient and activity coefficient are calculated using the Peng-Robinson cubic EOS (Peng and Robinson, 1976).

### 2.2.6 Diffusion Coefficient

The commonly used forms for the molecular diffusion coefficient are based on the Stefan-Maxwell relationship (SM) and Fick’s law. The former gives the Stefan-Maxwell coefficient $\varphi$ while the latter calculates the Fickian coefficient, $D$. The two types of diffusion coefficient are related to each other as we show in this section. In this work, we shall use the SM method as this method is easier to implement (see appendix A4 for a detailed computation). This coefficient is also required in the computation of the pressure and thermal diffusion fluxes.

For a non-ideal $n$-component mixture, the mole-based SM molecular diffusive flux is given by:

$$\left( \bar{J}^M \right) = -c[D^M](\nabla x)$$  \hspace{1cm} 2-11

where $D^M$ is Fick’s diffusion coefficient which is computed using Eq. 2-1:
\[ [D^M] = [B^M]^{-1}.[\Gamma] \]  

where \( B^M \) is a square matrix. The elements of \( B^M \) are given by (Amundson et al., 2003):

\[ B^M_{ij} = -\frac{x_i}{\varphi_{ij}}, \quad i = 1, \ldots, n, \quad i \neq j \]  

\[ B^M_{ii} = \sum_{k=1}^{n} \frac{x_k}{\varphi_{ik}}, \quad i = 1, \ldots, n, \]  

where \( \varphi_{ij} \) is the SM diffusion coefficient for each \( i-j \) binary pair in the mixture and \( x_i \) is the mole fraction of component \( i \). Note that for the SM diffusion coefficient, \( \varphi_{ij} = \varphi_{ji} \). In Eq. 2-11, \( \Gamma \) is the matrix of thermodynamic factors with elements described previously in Eq. 2-9. This parameter can either be calculated using activity coefficients which is obtained from equation of states. Many authors calculate \( \Gamma \) from activity coefficients, which can accurately describe the composition dependency of \( \Gamma \), but fail to represent the dependency on pressure (Leahy-Dios and Firoozabadi, 2007). The Peng-Robinson equation of state has a high accuracy for describing the non-ideality for hydrocarbon mixtures (Leahy-Dios and Firoozabadi, 2007).

To calculate the SM diffusion coefficient, we opt to use the correlation proposed by Kooijman and Taylor (1991) for multi-component mixtures based on a generalization of the Vignes equation for binary systems (Vignes, 1966). For a mixture of \( n \) components, this correlation reads:

\[ \varphi_{ij} = \left( D^\infty_{ij} \right)^{x_i} \left( D^\infty_{ji} \right)^{x_j} \prod_{k=1, k \neq i, j}^{n} \left( D^\infty_{ik} D^\infty_{jk} \right)^{x_k/2} \quad i, j = 1, \ldots, n \]  

where \( D^\infty_{ij} \) are the infinite dilution diffusion coefficients. We use the correlation proposed by Leahy-Dios and Firoozabadi (2007) to calculate the infinite dilution coefficients (see Appendix A4).
2.2.7 Interaction Effects

Recall that the diffusion flux of an \( n \)-component system can be expressed using \( n-1 \) governing equations as only \( n-1 \) equations are independent due to restriction of the driving forces; \( \sum_{i=1}^{n} \nabla x_i \). These characteristics are best illustrated by considering the total molecular diffusion flux for the binary system:

\[
J_1 = -cD_{12} \nabla x_1 \tag{2-16}
\]

For a ternary mixture, the molecular diffusion flux can be described explicitly by two equations:

\[
\begin{align*}
J_1 &= -cD_{11} \nabla x_1 - cD_{12} \nabla x_2 \\
J_2 &= -cD_{21} \nabla x_1 - cD_{22} \nabla x_2 \tag{2-17}
\end{align*}
\]

where \( D_{ij} \) are the elements of the Fick diffusion coefficients. From the equation above we see there is the possibility that component \( i \) may have a negligible driving force (compositional gradient) but still have a significant diffusion flux, \( J_i \). The cross-diffusion terms in the Fickian diffusion coefficient, \( D_{ij} \) are generally non zero, thus the flux may arise due to the compositional gradient of the other component. This phenomenon is referred to as osmotic diffusion (Toor, 1957).

Another interesting phenomenon that arises in multi-component diffusion is the diffusion barrier (Toor, 1957). This arises when component \( i \) does not diffuse at all even though the driving force for this species is not negligible. For example in a ternary system, this occurs when the two terms in the right hand side of Eq. 2-16 are equal in magnitude but have different signs. This leads to a zero diffusion flux. Finally, species \( i \) can diffuse in the opposite direction to that predicted by its compositional gradient. This is referred to as reverse diffusion (Toor, 1957). This occurs when the product of the cross diffusion term and the driving force is bigger in magnitude than that of the self diffusion terms.

\[
J_i / (-\nabla x_i) < 0, \quad (D_{ii} \nabla x_i < D_{ij} \nabla x_j) \tag{2-18}
\]

The cross diffusion effects do not occur in binary mixtures or multi-component mixtures where the non-diagonal terms in the Fick’s coefficients are approximately zero. It only occurs in systems where the binary diffusion coefficients are similar, for example oxygen-nitrogen-
carbon monoxide mixture, as well as mixtures where one species is present in large excess (Taylor and Krishna, 1993).

Figure 2-2 shows a schematic that illustrates these interaction effects; we plot the diffusion flux as a function of $-\nabla x_i$ for a binary and a hypothetical ternary system. Fick’s diffusion coefficients and the gradient of the component $2, \nabla x_2$ are considered independent for the purpose of this diagram. For the binary mixture, notice that the line passes through the origin while for a ternary system the line that represents Eq. 2-16 is shifted up or down to an extent depending on the magnitude and sign of $D_{12} \nabla x_2$.

![Figure 2-2: Diffusion flux as a function of compositional gradient for a binary and ternary systems](Modified from Taylor and Krishna, 2003).
2.3 Natural Convection

In addition to diffusion, bulk movement of fluid due to density gradients also occurs in hydrocarbon reservoirs. These density gradients maybe established by temperature and/or concentration gradients. This bulk movement is referred to as convection. The concentration-driven convection is also known as density driven overturning; while temperature driven convection is sometimes referred to as thermal convection. We have previously discussed about how a vertical temperature gradient occurs in most reservoirs due to the natural geothermal gradient. Horizontal temperature gradients can also arise in the subsurface due to non-uniform thermal conductivity in the reservoir rocks.

Natural convection due to density gradients are frequently inherited from the reservoir filling history. The initial fluids expelled from the source rocks are relatively dense liquids. As a source rock becomes more thermally mature, it expels progressively lighter fluids and eventually gases. The segment of the reservoir closest to the source kitchen has often received the latest, lowest density discharge. Field observation confirms this. For example, England et al., (1995) show that this is the case in the Forties, where the most mature kitchen is located to the side of the reservoir. This would lead to a density difference across the field. Figure 2-3 shows the process of density driven convection in a hypothetical rectangular reservoir. Starting with the denser fluid in the right hand part, and as time progresses the interface remains linear (if the viscosity does not change with density and the viscosity ratio is close to unity) and gradually moves by tilting towards equilibrium, horizontal position. This will result in the denser fluid moving to the bottom of the reservoir and the lighter fluid migrating to the top.

The bulk flow of fluid due to natural density driven convection in the subsurface is governed by the continuity equation:

$$\nabla \cdot (cv) = 0$$  \hspace{1cm} (2-19)

where the velocity is given by Darcy’s law,

$$\dot{v} = -\frac{k}{\mu} (\nabla P + \rho \bar{g} \nabla z)$$  \hspace{1cm} (2-20)
Note that in Eqs. 2-18 and 2-19, $\tilde{v}$ is the true velocity.

Figure 2-3: Schematic of gravity overturning. The reservoir is initially filled with two fluids of different density separated by a vertical interface. Gravity leads to the rotation of the interface so that the denser fluids lie under the lighter one.

2.3.1 The Rayleigh Number

As already established, in-reservoir mixing of petroleum is believed to be caused by molecular diffusion or density-driven convection or a combination of the two processes. Whether the fluid column is likely to thermally convect or not might be deduced by the Rayleigh number (Ra) defined by Bories and Combarnous (1973). This is usually referred to as the Horton-Rogers-Lapwood problem. The Rayleigh number is a measure of the ratio of the thermal convection flux to the viscous forces, which tend to resist convection. The Rayleigh number is defined by:

$$Ra = \frac{\beta kg (\rho c_p)_f H^2 \Delta T}{\eta \lambda H}$$  \hspace{1cm} 2-21

where $\beta$ is the volumetric thermal expansion coefficient, $k$ is the permeability of the reservoir, $g$ is the acceleration due to gravity, $(\rho c_p)_f$ is the product of fluid density and the heat capacity, $H$ is the thickness, $\frac{\Delta T}{H}$ is the thermal gradient, $\eta$ is the kinematic viscosity and $\lambda$ is the thermal conductivity of the medium. For a pure fluid heated from below, if the $Ra$ is greater than $4\pi^2$ (c. 40), convection will occur in the system (Nield and Bejan, 2013).
The use of Rayleigh number has been extended to cover both vertical ($Ra_v$) and horizontal ($Ra_H$) temperature profiles. Using the values of the parameters in the above equation similar to those found at reservoir conditions, Horstad et al., (1990) established that convection due to normal vertical thermal gradients would not readily occur in reservoirs. The reservoir must be unusually thick for thermal convection to occur, even in a highly permeable reservoir. However, there is no critical Rayleigh number for reservoirs with lateral temperature gradients and thermal convection may then become important (Jacqmin, 1990).

The concept of Rayleigh number has also been extended to systems with both compositional and thermal gradients (see Fig. 2-4); here the Rayleigh number is referred to as the solutal Rayleigh number ($Ra_s$). $Ra_s$ is the product of the Rayleigh number, the buoyancy ratio and the Lewis number.

$$Ra_s = \frac{g \alpha k H \Delta c}{\eta D_m} = N \cdot Le \cdot Ra$$  \hspace{1cm} (2-22)

The reader is reminded that $\alpha$ and $D_m$ are defined as the thermal expansion coefficient, and the mass diffusion coefficient, respectively. The Lewis number and the buoyancy number are defined by the equations below:

$$Le = \frac{\lambda}{D_m (\rho c_p)_f}$$  \hspace{1cm} (2-23)

$$N = \frac{\beta_c \Delta c}{\beta \Delta T}$$  \hspace{1cm} (2-24)

where $\Delta C$ is the concentration difference across the system, $c_p$ is the heat capacity of the fluid and $\beta_c$ is the concentration expansion coefficient.

Due to the complex nature of the convection problem for a system driven by composition and thermal differences, it is impossible to solve the general problem analytically. However, simplified cases have been studied extensively and analytical solutions have been derived for simple boundary conditions (Nield and Bejan, 2013). These previous studies use stability analysis to determine the limit of parameters that would lead to the Rayleigh number exceeding its critical value in which case point convection occurs in these simple models. For a simple 2D model with a vertical temperature and composition gradient similar that found in
a petroleum reservoir (see Fig.2-4), the onset of convection occurs when the \( \text{Ra}_s + \text{Ra} \geq 4\pi^2 \). A number of authors have investigated more complicated systems (Lage and Neild, 1998 and Manole et al., 1994) and provided critical values for these cases.

There is a substantial body of work investigating the combined effects of convection and diffusion. However, the majority of the research focuses on the onset of convection due to vertical thermal heterogeneity large enough to generate instabilities and induce convection (Bedrikovetskii et al., 1993). This kind of study is distantly related to our work and as mentioned in this section, thermal convection due to vertical geothermal gradients does not occur readily. In this work, we consider thermal convection due to lateral temperature gradients and are unconcerned with the Rayleigh stability check.

![Figure 2-4: Simplified 2D porous media with linear compositional and thermal gradients (Nield and Bejan, 2013).](image)

### 2.4 Compartmentalization

Reservoir compartmentalization is a key issue that has to be dealt with in the oil and gas industry during appraisal phase; and this plays a very important factor in determining an economically viable recovery process and development plan for the field. A reservoir is referred to as compartmentalized when it has barriers present that impede the flow of the hydrocarbons in the subsurface. These barriers subdivide the reservoirs into different unconnected sections. Late identification of these barriers or missing them completely can be detrimental to the economics of the project, as this will drastically reduce the oil or gas recovery. A reservoir can be compartmentalized by laterally extensive poor reservoir rock
such as shale layers, carbonated cemented zones or tar mats (Smalley and England, 1994) or faults. These barriers can either prevent flow completely or act as baffles to fluid flow.

Smalley et al., (1995 and 2004), Smalley and Muggeridge (2010) and Muggeridge et al., (2004) studied the mixing rates for the four main types of reservoir fluid data available: fluid pressure, fluid contacts, fluid density and fluid composition. The timescale required for both the fluid contacts and fluid density to reach equilibrium was obtained from the analytical solution first derived by Gardner et al., (1962). This process is governed by density driven convection. The timescale for the complete mixing of two, initially segregated, miscible fluids in a porous medium via molecular diffusion was first presented by England et al. (1987). The time taken for normal pressures to dissipate over a distance $L$ in the absence of a barrier is presented by Smalley et al., (2004). In the studies above, these equations were used to calculate the mixing times of the difference fluid variations to a range of simple fluid scenarios. They found that the different fluid properties have significantly different steady state timescales which goes in the order: diffusion > fluid density > fluid contacts > fluid pressure. The expressions for the “order of magnitude” mixing times and their typical ranges can be computed using the effective diffusion coefficient presented by Smalley and Muggeridge (2010) shown in Table 2-1. The ranges of effective diffusivities in Table 2-1 are obtained using a simple reservoir model with a length and porosity of 1000m and 0.2, respectively, for different hydrocarbon fluids with typical disturbances in the fluid properties. Using the effective diffusivity, for a typical reservoir length (200 m) from this table, we see that the pressure differences tend to reach equilibrium in a matter of years, while gravitational overturning which governs density variations and fluid contacts may take about thousands of years to equilibrate and the timescales for fluid composition to mix via molecular diffusion will take about millions of years depending on the length scale.
Table 2-1: Estimates of timescales for the diffusion (molecular and pressure) and density driven natural convection (gravity overturning). The ranges of the effective diffusion coefficient of each process are also presented (Adapted from Smalley and Muggeridge, 2010).

<table>
<thead>
<tr>
<th>Timescales (seconds)</th>
<th>Effective diffusion coefficient, D_e (m^2 s^-1)</th>
<th>Range of D_e for k = 100mD (m^2 s^-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure</td>
<td>$\frac{H^2 \mu \phi c_e}{2k}$</td>
<td>$\frac{2k}{\mu \phi c_e}$</td>
</tr>
<tr>
<td>Gravitational overturning</td>
<td>$\frac{25H^2 \mu \phi}{4k g H \Delta \rho}$</td>
<td>$\frac{4k g H \Delta \rho}{25 \mu \phi}$</td>
</tr>
<tr>
<td>Molecular diffusion</td>
<td>$\frac{H^2 \tau}{D}$</td>
<td>$\frac{D}{\tau}$</td>
</tr>
</tbody>
</table>

As described earlier, it is commonly assumed that spatially varying fluid properties signify that a reservoir contains barriers. However, this might also be an indication that the fluid property has no equilibrated to steady state. In reality it might take a very long time for these properties to reach steady state after the process that led to perturbation has stopped. In this thesis, these analytic expressions presented will be used to provide a preliminary estimate for timescales that are suitable for comparing with the age of the event that led to the disturbances in fluid properties (or the reservoir age) to infer whether the reservoir is actually compartmentalized or is still in the process of attaining steady state.
Chapter 3

Investigation of Vertical Composition Variation in One Dimensional Hydrocarbon Reservoirs

In a one-dimensional domain the convection flux is absent, thus the diffusive fluxes alone shape the fluid distribution. The combined effect of thermal diffusion and gravity segregation (a combination molecular and gravity diffusion) in the one dimensional vertical direction has been well studied. Galliero and Montel (2008 and 2009) used molecular dynamics simulations along with an equation of state (EOS) to study the effect of the diffusion processes on the transient and steady state fluid distribution in isotopic mixtures. More recently, Jospeh and Imo-Jack (2013) used the one dimensional diffusion modelling to predict whether a significant oil-rim was present in the Niger Delta fields.

In this chapter, we investigate the effect of the individual diffusional fluxes on the fluid mixing process and how they shape the steady state compositional profile and the equilibrium timescales. We start off by describing the governing equations for diffusional fluid mixing in a one dimensional vertical column for single-phase mixtures and then outline how they can be solved numerically. We then present a new analytical solution to determine the steady state compositional profile for fluid mixtures under the influence of pressure and molecular
diffusional fluxes. The numerical and analytical solutions are then used to reproduce and study the unusual mixing trends in the ternary systems studied by Ratulowski et al., (2003).

3.1 Conservation Equation for Diffusive Mixing

For a one-dimensional domain the convective flux does not play a part in the species distribution, hence for a vertical column the conservation equation for a multi-component mixture can be written as:

\[
\frac{\partial \bar{c}}{\partial t} = -\frac{\partial \bar{J}^M}{\partial z} - \frac{\partial \bar{J}^p}{\partial z} - \frac{\partial \bar{J}^T}{\partial z}, \quad i = 1, ..., n
\]  

where \( \bar{c} \) is a vector whose components are the molar concentration of each component and \( \bar{J}^M \), \( \bar{J}^p \) and \( \bar{J}^T \) are vectors of the molecular, pressure and thermal diffusion flux, respectively. In this chapter, we will place more emphasis on molecular diffusion as this phenomena has been well studied compared to the other diffusion fluxes. It is convenient to express the diffusion fluxes in a matrix form, as illustrated among others by Taylor and Krishna (1993), who show the derivation of diffusion fluxes in detail. The molecular diffusion flux is computed by the Eq. 3-2:

\[
\bar{J}^M = -c[D^M](dx/dz)
\]  

where \( \bar{J}^M \) is a vector of the molecular diffusion flux for all species and \( dx/dz \) is a vector of the mole fraction gradient of all components. The Fickian diffusion coefficient \( [D^M] \) governs the timescale for mixing by molecular diffusion. The reader is reminded that in the computation of the diffusive flux that the variation in the overall composition in the system is negligible compared to the variation in composition, hence the overall concentration can be assumed to be constant.

Firoozabadi (1999) presented the derivation for pressure driven diffusion based on Gibbs sedimentation equation. In a system in vertical equilibrium, this is referred to as gravity
diffusion as the diffusion process is now under the influence of gravity. The driving force for the gravity diffusion for each component can be expressed in vector form as:

$$ \overline{G^P} = \begin{bmatrix} \frac{x_1(\rho v_1 - M_1)g}{RT} \\ \vdots \\ \frac{x_n(\rho v_n - M_n)g}{RT} \end{bmatrix} $$

where $v_i$, $M_i$, $g$, $R$, $T$, and $\rho$ are the molar volumes of species $i$, molecular weight of species $i$, acceleration due to gravity, the universal gas constant, temperature and mass density respectively. The gravity diffusion flux can be expressed in a similar form to that used by Taylor and Krishna (1993) to express the molecular diffusion:

$$ \overline{j^P} = c[B^M]^{-1}\overline{G^P} $$

where $\overline{j^P}$ is a vector of the gravity diffusion flux for all species and $[B^M]$ is a matrix whose elements are defined by Eq. 2-12 and 2-13 in the previous chapter.

In non-isothermal systems, the driving force of the thermal diffusion process is the product of the thermal diffusion ratio multiplied by the derivative of the natural logarithm of the geothermal gradient. The equation for the thermal diffusion flux is expressed in vector form by:

$$ \overline{j^T} = -c[B^M]^{-1}(\overline{\kappa_T}), \left(\frac{d\ln T}{dz}\right) $$

where $\overline{\kappa_T}$ is a thermal diffusion ratio vector. This term is a measure of the thermal diffusion. The sign convention of $\overline{\kappa_T}$ determines the direction of thermal diffusion. The reader is reminded that, in this work, a positive thermal diffusion ratio will indicate the migration of component $i$ to the (hot region) bottom of the reservoir. In the numerical solution developed in the next section, we assume that this parameter is independent of composition. We use values obtained from either experiments or results from other numerical models. This assumption simplifies the computation of the diffusive flux; however it is important to note that this parameter is dependent on mole-fraction as shown in Shukla and Firoozabadi (1998).
It is key to note that in order to calculate the diffusive flux; we multiply the diffusion coefficient by the driving force of the respective flux. For the molecular diffusion process, we multiply the driving force, the compositional gradient, by the Fick’s diffusion coefficient to account for the non-ideality of the fluid. The thermal and pressure diffusion fluxes are however calculated by multiplying the respective driving forces by the Stefan-Maxwell diffusion coefficient.

### 3.2 Numerical Method for a 1D Domain

#### 3.2.1 Mathematical Model

In order to study how the compositions of each component in a given mixture changes over time due to molecular, pressure and thermal diffusion, we have to solve Eq. 3-1. This cannot be done analytically; we therefore developed a computer program to solve this numerically. In this work, we use the finite volume method for a 1D reservoir of thickness $H = 2L$, with spatial position $-L \leq z \leq L$. The discretisation of Eq. 3-1 using finite volume is shown below:

![Figure 3-1: Grid orientation for the one-dimensional domain.](image-url)
This breaks down to:

\[
\frac{1}{\delta t} \int_k^{k+1} \int_z^{z+1} \frac{\partial \tilde{c}}{\partial t} \, dz \, dt = - \left( \frac{1}{\delta t} \int_k^{k+1} \int_z^{z+1} \left( \frac{\partial J^P}{\partial z} + \frac{\partial J^M}{\partial z} + \frac{\partial J^T}{\partial z} \right) \, dz \, dt \right) \tag{3-6}
\]

where \( k \) represents the time-step, \( \delta t \) is the time step size, \( \delta z \) is the grid size, \( z \) is the grid point, \( \tilde{c}^k \) is a vector whose elements are the molar concentrations of the each component in the \( z \) grid point at the \( k \)th time-step and \( \left( J^k \right) \) is a vector whose entries are the molecular, thermal or pressure diffusion flux. In order to solve for the steady state solution, we advance forward with time from the initial composition profile by solving Eq. 3-7 explicitly to obtain \( c_{z+1/2} \) at the \( k+1 \) time instant. For the ease of debugging the code, we use an explicit operator-splitting scheme where the diffusive fluxes are solved independently. This is achieved by creating separate functions to implement the molecular, pressure and thermal diffusion problem separately. We first solve the molecular diffusion problem:

\[
\frac{c^{k+1}_{z+1/2}}{\delta t} - \frac{c^k_{z+1/2}}{\delta t} = - \left( \frac{\partial J^M}{\partial z} \right)_{z+1/2} - \left( \frac{\partial J^M}{\partial z} \right)_{z} \tag{3-7}
\]

The (*) represents the concentration obtained after molecular diffusion for each time-step. For gravity diffusion we have:

\[
\frac{c^{k+1*}_{z+1/2}}{\delta t} - \frac{c^{k*}_{z+1/2}}{\delta t} = - \left( \frac{\partial J^P}{\partial z} \right)_{z+1/2} - \left( \frac{\partial J^P}{\partial z} \right)_{z} \tag{3-9}
\]

The (***) represents the concentration obtained after pressure diffusion for each time-step. Finally, for thermal diffusion we have:
Recall, we assume our systems have no source or sinks. Thus we impose a no flux boundary condition:

\[ c_{z+1/2}^{k+1} = c_{z+1/2}^{k*} - \delta t \left( \frac{\partial f_i^T}{\partial z} \right)_z^k \left( \frac{\partial f_i^T}{\partial z} \right)_z^{k*} \]  

3-10

We seek the steady state solution and we advance the numerical solution with time until equilibrium is reached. In this work, convergence to the steady state is assumed when the percentage change in mole fraction of all components is less than \( 10^{-6} \) between two successive iterations at each grid point except when stated otherwise.

### 3.2.2 Initial Conditions (Reservoir Initialization)

Along with boundary conditions, appropriate initial conditions are required to complete the one dimensional multi-component formulation. The domain is initialized assuming vertical pressure equilibrium throughout this study. However, we impose either a constant or varying composition or temperature distribution on our system to initialize the domain.

#### 3.2.2.1 Mole Fractions

Three types of initial conditions are implemented in our one-dimensional multi-component numerical model. They include

- Uniform mole fractions with depth across the reservoir,
- Step function-like mole fraction variation and
- Uniform gradient of the mole fraction with depth.
These three cases can be related to different reservoir filling scenarios:

- Case 1: This indicates a scenario were the reservoir is charged relatively fast, thus the composition does not change throughout the filling process.
- Case 2: The reservoir is filled with one fluid then later charged with another fluid from another source rock, and so has a different composition.
- Case 3: This arises from the gradual fluid charging of a reservoir that already contains a fluid. This can also arise due to normal fluid charging of a reservoir from a single source; as the source rocks matures it expels lighter fluids.

Fig. 3-2 shows the three cases for the initialization of a simple binary mixture. As, the steady state is independent of the initial conditions used the three initial conditions shown here will give the same steady state solution as long as the initial number of moles is the same.

![Diagram showing different reservoir initial conditions](image)

**Figure 3-2: Different reservoir initial conditions for the numerical simulations. The graph relates the mole fraction (solid line) as a function of reservoir depth \((-l \leq z \leq l\). From left to right: uniform mole fraction with depth, step function like distribution and the case where there is a uniform mole fraction gradient in the domain.**

### 3.2.2.2 Reservoir Temperature Gradient

In order to study the effect of thermal diffusion, we impose a temperature gradient in the system. The temperature field is assigned initially in the domain and remains constant throughout the simulations as opposed to including the energy equation, as we wanted to
study the effect the imposed temperature gradient would have on our system via thermal diffusion. The temperature field is initialized with the Eq. 3-12:

$$T = T_x(z - z_0) + T_0,$$

3-12

where $T_x$ is the geothermal gradient while $T_0$ and $z_0$ are the temperature and depth at the reference point.

### 3.2.3 Numerical Stability

Numerical stability means that errors at any stage of the computation are not amplified but are attenuated as the computation progresses. Implicit methods are always stable. However, in explicit methods like in the one implemented in this work, the result may be numerically unstable due to use of large time steps for a given grid size. Thomas (1995) showed that the explicit finite volume (or finite difference) solution of the two dimensional PDE is both convergent and stable if the ratio of the time step ($\delta t$) and a square of the grid size ($\delta z^2$) is less than some maximum value. This ratio is referred to as the Courant-Friedrichs-Lewy condition after the authors who initially described it in their 1928 paper.

The stability criterion for the molecular and thermal diffusion process is found by:

$$\delta t_D = \frac{(\delta z)^2}{2D_{max}^M}$$

3-13

where $\delta t_D$ is the maximum stable time step for molecular diffusion and $D_{max}$ is the largest absolute value of the elements of the Fickian diffusion coefficient matrix $[D^M]$ among all spatial points at the current time step. The stability criterion for the gravity diffusion process is defined by

$$\delta t_P = \frac{\delta z}{A_{max}}$$

3-14

where $\delta t_P$ is maximum time step and $A_{max}$ is the largest value of the vector $\frac{1}{RT} [B^M] \frac{\delta G^P}{\delta x_i}$ among all grid points at the current time step. The time step used for the numerical simulations was determined by the minimum of these two stability criteria at each time step.
\[
\delta t = \min(\delta t_D, \delta t_p)
\]

3.3 Analytical Solution

The transient analytical solution for the mass conservation equation for the individual diffusion fluxes in 1D has been well discussed by Crank (1975) for molecular diffusion and Carslaw and Jaeger (1959) for conduction of heat in solids. Analytical solution for the steady state of a multicomponent mixture under the influence of the three diffusive fluxes has been derived for simplified isotopic mixtures by Galliero and Montel (2008). The steady state composition solution for an ideal multicomponent system under the influence of pressure and molecular is also well known (Firoozabadi, 1999). These analytical solutions serve us as means to validate the conclusions from the numerical model we developed. The short coming of the present steady state compositional profile analytic solution is that it requires prior knowledge of the composition at a reference position in the domain to calculate the composition at the other positions or nodes. In this section, we present the derivation of the analytical solution for a mixture under the influence of molecular and pressure diffusion; and then present our new analytical solution based on mass conservation in the one-dimensional domain.

A static multi-component fluid subject to a gravitational field in one dimension has been known to develop compositional gradients through the process of diffusion (Firoozabadi, 1999). In thermodynamic equilibrium, the mole fraction of the denser fluids decreases with increasing height. When an isothermal \(n\)-component mixture is subjected to a constant gravity field (in the \(z\) direction), one can calculate analytically the equilibrium distribution of the species by recalling the fact that the total potential of each component is constant (Gibbs, 1957).

\[
\left(\frac{d\mu_i}{dz}\right)_T = -M_i g,
\]

where \(\mu_i\) is the chemical potential, \(M_i\) is the molecular weight, and \(g\) is the acceleration due to gravity. The above equation can be used to solve for the compositional variation in a one-dimensional domain as long as the composition of the species at a reference point is known.
To solve the equation (3-16) analytically, we make use of thermodynamic result that for an isothermal \( n \)-component mixture,

\[
d\mu_i = v_i dp + \sum_{j=1}^{n-1} \frac{\partial \mu_i}{\partial x_j} dx_j,\tag{3-17}
\]

where \( v_i \) is the molar volume and the \( x_i \) is the molar fraction of component \( i \). For Ideal mixtures,

\[
\mu_i = RT \ln x_i + A\tag{3-18}
\]

where \( R \) is the universal gas constant and \( A \) is a constant that represent the chemical potential of the pure species \( i \) at standard pressure. Substituting the above expression into Eq. (3-17) we obtain:

\[
d\mu_i = v_i dp + RT \frac{dx_i}{x_i} \tag{3-19}
\]

Recall that we assume a system under vertical pressure equilibrium, thus:

\[
\frac{dp}{dz} = -\rho g, \tag{3-20}
\]

where \( \rho \) is the mass density. By combining the above equations we obtain:

\[
\frac{RT}{x_i} \frac{dx_i}{dz} = (\rho v_i - M_i)g \tag{3-21}
\]

One of the key assumptions made by Firoozabadi (1999) when he derived the above expression was that the system was isothermal. Thus the solution above would only account for pressure (gravity) and molecular diffusion. Eq. 3-21 forms the basis of the analytical solutions found in literature for the steady state composition in a one dimensional gravitationally segregated system.

For a reservoir of height \( 2L \) where the \( -L \leq z \leq L \), the steady state mole fraction of each component at any point along the vertical thickness of the reservoir can be calculated analytically, provided the composition at a reference point is known. If we use the bottom of the reservoir as the reference point, integrating Eq. 3-21 we obtain:
\[ x_{i(z)} = x_{i(-L)} \exp\left[ (\rho_{av} v_i - M_i) \left( \frac{g}{RT_{(-L)}} \right) (z + L) \right] \]  

where \( \rho_{av} \) is the average density of the mixture in the domain. This solution has been around for some time and has been used by various authors to validate both their experimental and numerical work. Galliero and Montel (2008) used a simplified version of this solution to validate their molecular dynamics simulations for simple Lennard-Jones mixtures under the influence of gravity. More recently, Touzet et al., (2011), used this solution to validate their isothermal microgravity experiments and molecular dynamic simulations on a synthetic ternary mixture of methane, \( n \)-butane and \( n \)-dodecane at typical petroleum reservoir conditions i.e. high temperatures and pressures. The aim of their work was to highlight the importance of thermo diffusion on the vertical distribution in the fluid column by comparing the isothermal and non-isothermal steady state distributions.

The afore mentioned studies show that solutions given by Eq. 3-22 works well, however it does require a prior knowledge of the steady state composition of each component at one point before it can be used. It would be better if we could predict the steady state analytic solution without having to carry out numerical simulations or experimental work beforehand; we thus propose to improve the current solution.

### 3.3.1 Applying Mass Conservation to the above Analytical Solutions

One of the main assumptions made in this work is that there are no sources or sinks in our reservoirs, therefore the mass should be conserved i.e. the total number of moles in the system should be the same at any point of the mixing process. The number of moles of component \( i \) in the system at steady state should be same at the initial state (or at any transient state) of the mixing process which is known:

\[
\int_{-L}^{L} x_{i(-L)} \exp\left[ (\rho v_i - M_i) \left( \frac{g}{RT_{(-L)}} \right) (z + L) \right] dz = \int_{-L}^{L} x_i^0 dz, \tag{3-23}
\]

where \( x_i^0 \) is the initial mole-fraction of component \( i \). Assuming the mass density variation in the reservoir is negligible, we obtain (hence the approximation sign in Eq. 3-24):

\[
x_{i(-L)} \left[ \left( \frac{\exp(2\theta_i L) - 1}{\theta_i} \right) \right] \approx \int_{-L}^{L} x_i^0 dz, \tag{3-24}
\]
where $\theta_i$ is defined as

$$\theta_i = \frac{\rho_{av} v_i - M_i}{RT_{(-L)}} g$$  

3-25

Substituting Eq. 3-24 into Eq. 3-22 we obtain:

$$x_{i(z)} \approx \int_{-L}^{L} x_i^0 \, dz \left( \frac{\exp(2\theta_i L) - 1}{\theta_i} \right) \exp[\theta_i(z + L)]$$  

3-26

The above expression forms the basis of a new steady-state solution for an ideal mixture under the influence of molecular and gravity diffusion in a closed reservoir. It should be noted that the composition at any time of the mixing process can also be used to compute $\int_{-L}^{L} x_i^0 \, dz$; however in this work we shall use the initial composition profile. For the simplest of the three initial conditions described in the previous section (Case 1 where the initial distribution $x_i^0$ is constant throughout the reservoir) one can solve the integral easily and obtain

$$x_{i(z)} \approx \frac{2x_i^0 L}{\exp(2\theta_i L) - 1} \exp[\theta_i(z + L)]$$  

3-27

Besong (2010) derived Eq. 3-27 for 1D systems with initial uniform compositions. We improve upon this by extending the analytical solutions for the other two initial reservoir conditions considered in this work, where $x_i^0$ is not constant. As mass is conserved in these cases, we replace the initial composition for component $i$ term in Eq. 3-27 with the average distribution of the mole-fractions for component $i$ at the initial state of the reservoir $\overline{x_i^0}$. Thus,

This can be calculated by:

$$\overline{x_i^0} = \frac{\int_{-L}^{L} c x_i^0 \, dz}{\sum_{i=1}^{n} \left( \int_{-L}^{L} c x_i^0 \, dz \right)}$$  

3-28

The new analytical solution is thus computed by:
\[ x_{i(z)} \approx \frac{2x_i^0 L}{\exp(2\theta_i L) - 1} \exp[\theta_i(z + L)] \]  

3-29

See Appendix A2 for a more detailed derivation of the term \( x_i^0 \) used for the analytical solution for the two initial conditions where the composition varies in the reservoir.

Recall that the key assumptions made for the derivation of the analytic solution is that the density does not vary much in the reservoir at steady state. The separation-mixing process does not always equilibrate to an approximate uniform mixture. In this case, there will be separation of each component \( i \) in the reservoir leading to a density difference at steady state.

### 3.3.2 Analytical Approximation for Separation

In this section we derive an expression to predict the steady-state segregation of an ideal fluid under the influence of gravity and molecular diffusion based on the analytical solution described in section 3.3.1. We define the separation of a component \( i \) in the reservoir as the difference in the mole fraction at the top and the bottom.

\[ S_i = x_{i(L)} - x_{i(-L)} \]  

3-30

where \( S_i \) is the a measure of the vertical segregation in the reservoir. Describing the composition at the top and bottom of the domain in a similar way to Eq. 3-29, we obtain an expression to predict the isothermal compositional grading for an ideal fluid mixture:

\[ S_i = \frac{2x_i^0 L}{\exp(2\theta_i L) - 1} (\exp(2\theta_i L) - 1) = 2L \theta_i x_i^0 \]  

3-31

The above expression shows that the segregation in an isothermal system under the influence of gravity and molecular diffusion, the separation is directly proportional to the thickness of the reservoir and the term \( \rho_{av} v_i - M_i \). It is however not directly proportional to \( x_i^0 \) because \( \rho_{av} \) is dependent on this parameter.
3.3.2.1 Separation for Real Mixtures

For non-ideal systems, we include the thermodynamic factor in the driving force for the molecular diffusion flux and we can express Eq. 3-21 in vector form:

$$\left[\Gamma\right] \frac{d}{dz} \ln(\bar{x}) \approx \bar{\theta}$$  \hspace{1cm} 3-32

When we integrate this expression we obtain:

$$\ln(\bar{x}) \approx \left[\Gamma\right]^{-1} \bar{\theta} z + \bar{A}$$  \hspace{1cm} 3-33

where \( \bar{A} \) is a vector constant of integration. If the integration is performed within the limits \(-L \leq z \leq L\), we get the expression:

$$x_{i(L)} \approx x_{i(-L)} \exp \sum_{j=1}^{n-1} \left(\Gamma^{-1}_{ij} \theta_j\right) 2L$$  \hspace{1cm} 3-34

If we repeat the procedure from section 3.3.2 the approximate separation in a real mixture can be calculated as:

$$S_i \approx 2L \bar{x}_i^0 \sum_{j=1}^{n-1} \left(\Gamma^{-1}_{ij} \theta_j\right)$$  \hspace{1cm} 3-35

It is important to note that this is an approximate solution as we have assumed that the elements in the thermodynamic factor are approximately constant within the range of concentrations we deal with at steady state. Eq. 3-35 reduces to Eq. 3-31 if we assume that the mixture is ideal, as the inverse of the thermodynamic factor is an identity matrix.

3.4 Test of the Numerical Method

A computer program was written to implement the numerical solution explained in the previous section (3.2). To validate the computer program, we test it against analytical solutions. We initially test the molecular diffusion part of the computer program against
analytical solution, and then we test the full program against an explicit steady state analytical solution.

When dealing with ideal mixtures ($\Gamma = 1$) whose components have the same molar volumes, the molecular diffusion equation is analogous to equation of the conduction of heat in solids. In this test, we model numerically the molecular diffusion mixing of a binary mixture that has a constant total concentration (as a result of equal molar volumes of the species). For a binary system under the influence of molecular diffusion the diffusion of species is governed by:

$$\frac{\partial c_A}{\partial t} = -\frac{\partial}{\partial z} \left( c_t D_{AB} \frac{\partial x_A}{\partial z} \right)$$ \hspace{1cm} 3-36

For an equi-molar volume system, this simplifies to:

$$\frac{\partial x_A}{\partial t} = D_{AB} \left( \frac{\partial^2 x_A}{\partial z^2} \right)$$ \hspace{1cm} 3-37

Carslaw and Jaeger (1959) present analytical solutions to Eq. 3-37; for different initial and boundary conditions. We compare the analytical solution of Eq. 3-37 with an initial condition of type 2 (step-function mole fraction variation) in a 1D domain with thickness of $H = 2L$ and spatial position of $0 \leq z \leq H$ with an imposed no flux boundary conditions to the simulations obtained from our computer program. The initial condition is represented by:

$$x_A(z, 0) = x_A^0 = \begin{cases} 1 & \text{for } 0 \leq z \leq L \\ \text{and} & \\ 0 & \text{for } L \leq z \leq H \end{cases}$$ \hspace{1cm} 3-38

where $L$ is half of the reservoir thickness, $H$ (see Fig. 3-1). The boundary condition for the closed reservoir is:

$$\frac{\partial x_A}{\partial z} = 0, \text{ at } z = 0 \text{ and } z = H$$ \hspace{1cm} 3-39

The analytical solution with for the above initial and boundary conditions is presented in Carslaw and Jaeger (1959):

$$x_A(z, t) = A_0 + \sum_{n=1}^{\infty} A_n \cos(k_n z) e^{-k_n D_{AB} t}$$ \hspace{1cm} 3-40
where \( k_n = \frac{n\pi}{H} \)

The Fourier series coefficients are given by

\[
A_0 = \frac{1}{H} \int_0^H x_A^0(z)dz, \quad A_n = \frac{2}{H} \int_0^H x_A^0(z) \cos \frac{n\pi}{H} \, dz \tag{3-41}
\]

where \( x_A^0(z) \) is the initial composition variation. When \( x_A^0(z) \) is a step function (second plot in Fig. 3-2), we obtain:

\[
A_0 = 0.5, \quad A_n = \frac{2}{n\pi} \sin \frac{n\pi}{2} \tag{3-42}
\]

We used the above equations to test our numerical simulation by comparing the transient and steady state profiles. We used an ideal binary fluid mixture of methane and \( n \)-decane with the same molar volume to carry out this exercise. A constant diffusion coefficient \( D_{AB} \) of \( 1.12 \times 10^{-8} \text{ m}^2\cdot\text{s}^{-1} \) was used within the domain of 304.8 m thickness. The reservoir dimension chosen for this exercise corresponds to that of the hydrocarbon reservoir which is used later on in our case study. Fig. 3-3 compares the numerical simulation from our computer program to the analytical solution of Eq. 3-37. The composition obtained from the analytical solution was plotted against the spatial position \(-L \leq z \leq L\) in order to compare this with the results obtained from our numerical simulations (Recall that the thickness of 1D reservoir \( H = 2L \)).

From Fig. 3-3, we observe that numerical solutions are in close agreement to the analytical solution proposed by Carslaw and Jaeger (1959). To quantify the match between the two solutions we plot the absolute deviation in Fig. 3-3. It can be observed that at early times \((t \approx 7,000 \text{ years})\), the maximum absolute deviation \((0.0035 \text{ for 21 grid-points})\) is higher than at late times \((0.00003 \text{ for 21 grid-points})\). The higher deviation at early times is due to the fact that discontinuous nature of the initial composition distribution. At late times, closer to steady state the compositional profile is no longer step-wise or discontinuous. The \( A_0 \) contribution dominates, thus the deviation decreases. The deviations in the mole-fraction can be reduced by refining the grid; this is evident in the right plots on Fig. 3-3(a), the deviation reduces at \( t \approx 7,000 \text{ years} \) from 0.0035 to 0.0004 when we increase the number of grid-points to 51.

We performed a grid-refinement exercise to demonstrate the clear convergence of our numerical scheme. Figure 3-3 (c) shows the errors in the steady state composition versus grid
refinement. The errors are plotted calculated as an average absolute deviation from the values obtained from the analytic solution. This plot shows that 21 grid points provides sufficient accuracy to model the diffusive mixing. We also investigated the impact of the reducing the time-step size will have on our simulations. This however does not change the results of our simulations (we arrive at the same steady state composition profile). This is because we used the CFL condition (Eq.3-15) to calculate the optimum time-step size. Any time-step size above this will lead to numerically unstable results, while smaller time-step sizes will increase the computational effort.

(a) \( t \approx 7,000 \) years

(b) \( t \approx 100,000 \) years
3.5 Test of the New Analytical Solution

In order to test the new analytical steady state solution for an ideal mixture under the influence of pressure and molecular diffusion, we opted to use a binary ideal fluid constituting of methane and \( n \)-decane as this mixture has been well studied and its properties are readily available in literature. We compare the new analytical solution against the results from our numerical simulations for two of the three initial conditions described in section 3.2.2 to prove that the different initial conditions would give the same steady state as long as the model is initialized with the same number of moles. Recall that the major assumption made whilst deriving this solution is that the density does not vary much within the reservoir. Therefore, we also test the validity of this approximation by comparing our analytical solution to molecular dynamic simulations carried out by Galliero and Montel (2008) where the force due to gravity affecting the segregation of the Lennard Jones Isotopes has been enhanced. This in turn leads to a greater steady state segregation and hence a non-uniform density distribution in the reservoir at steady state.

Figure 3-3: Comparison between the numerical and analytical solution for molecular diffusion only. The graphs on the left shows the mole fraction distribution of methane at different times in our simulation \((a) = 7000\) years and \((b) = 100,000\) years. \((\bullet = \text{Numerical simulation and the broken line = Analytical solution, both for 21 grid-points}).\) The plots on the right show the absolute difference between the two solutions at different times \((\circ = 21\ \text{grid-points and } \Delta = 51\ \text{grid-points}).\) (c) Error in steady state composition against grid refinement.
Table 3-1: Data used to simulate the methane/ n-decane mixture

<table>
<thead>
<tr>
<th>Fluid Mixture Properties</th>
<th>Methane</th>
<th>n-decane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (kg.mol⁻¹)</td>
<td>16.04 × 10⁻³</td>
<td>142.29 × 10⁻³</td>
</tr>
<tr>
<td>Molar volume (m³.mol⁻¹)</td>
<td>6.22 × 10⁻⁵</td>
<td>19.7 × 10⁻⁵</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>0.033</td>
<td>0.627</td>
</tr>
</tbody>
</table>

We obtained the properties of the components of the binary mixture simulated in both our analytic and numerical simulations at T = 393 K and P = 75 MPa from REFPROP 8.0 (Lemmon et al. 2007). Table 3.1 summarizes these properties. The thickness of the hypothetical reservoir was set to be 1000 m; this would be large enough to produce a reasonable segregation for comparison between the two solutions. The mixture is a single-phase fluid at the conditions studied (see Fig. 3-4a), as the pressure is far away from the phase envelope. As a measure of the non-ideality of the methane/n-decane mixture we compare the thermodynamic factors obtained from the Peng-Robinson EOS to that of an ideal mixture. Note that in this study, for an n-component fluid that the thermodynamic factor is represented by an n-1 by n-1 matrix. Hence for a binary mixture, the thermodynamic factor is represented by a scalar. In Fig. 3-4b, we plot the thermodynamic factor against the mole fraction of methane in the binary mixture. From this plot we conclude that the assumption that this mixture is ideal at T = 393 K and P = 75 MPa is valid as the thermodynamic factor is approximately equal to one.
Figure 3-4: (a) P-T phase envelope for the methane and n-decane mixture, (b) Thermodynamic factor of the binary mixture, these values are close to 1 for the varying mole-fractions of methane indicating that the fluid mixture is ideal.

For the initial conditions we initialized the reservoir with 40% methane and 60% n-decane. Fig. 3-5(a) shows the steady state composition of methane obtained for both the numerical and analytical solutions for the first case; where the domain was initialized with a uniform composition of the two components. In this case only 21 nodes or grid-points were used in the numerical simulation. At steady state as we expect, the top of the reservoir is enriched with methane the lighter component, while the heavier component (n-decane) segregate to the bottom of the reservoir. We can observe that the species distribution predicted by the analytical solution is an exact match with the numerical code, as the two plots overlap in Fig. 3-5(a). In order to represent the similarity between the two curves quantitatively, we plot the absolute difference between the curves in Fig. 3-5(b). These values are very small and with an average absolute deviation value of 0.01% between the two curves, we conclude that the analytical solution performs well at predicting the steady-state solution for the ideal binary mixture.
We also compare the steady state segregation of methane produced by the analytical and numerical solution curves to that computed by Eq. 3-31 derived in section 3.3.2 to test this expression. The differences in the methane mole fraction at the top and bottom of the reservoir for the analytical and the numerical model are 0.02864 and 0.02858, respectively. Assuming ideality of the binary mixture and computing (from Eq. 3-25) the value of $\theta_{CH_4} = 7.16 \times 10^{-5}$, we find that the segregation of methane in the reservoir by Eq. 3-31 is approximately 0.02864. The expression derived in Eq. 3-31 therefore provides a good approximation for predicting the separation of the species in the reservoir and can thus used as an initial test to check the validity of the numerical simulation produced in this study.

The second initial condition studied is that with a step-function like composition variation in the reservoir. In order for this case to give the same steady-state composition, the domain must be initialized with the same number of moles as the previous case. Using the more detailed version of Eq. 3-27 derived in Appendix A2, we find out that methane has to occupy about 17% of the total volume of the reservoir for the reservoir to have an average methane composition of 0.4. The analytical solution produces exactly the same solution as shown earlier. The numerical method simulated with only 21 grid-points will however have to be refined because this is not sufficient to accurately model the initial mole fraction with discontinuities present. We thus examined the influence of grid refinement on the segregation produced by our numerical simulations.
In Fig. 3-6(a) we observe that the segregation-mixing process initially simulated using 21 grid-points, reaches steady state at a lower composition to the analytical solution this means that the number of moles of methane in this system is reduced. The reduction in the number of moles occurs because of the number of grid points (21) is not sufficient to capture the discontinuity in the initial compositional profile accurately. We increased the number of grid points in the numerical simulation to obtain more accurate results. Fig. 3-7 shows the errors in the steady state composition versus the grid refinement. It can be observed from this plot that a sufficient amount of grid-points for this simulation is 121, as the simulation has reasonably converged. The steady state composition for the numerical simulation now matches the analytical solution. Fig. 3-8 shows the absolute difference between the two methods; these values are negligible and give an average absolute deviation (AAD) of 0.0012.

This exercise points out the main importance of the new analytical solution. The previous analytical solution is dependent on the knowledge of steady state composition at a reference depth. If the reference composition required for the analytic solution was obtained from the numerical simulation that converged to the wrong (inaccurate) solution like the case with 21 grid points (Fig.3-6(a)), the analytical solution would just complete the profile (giving the exact one to that produced by the numerical solution). Our new explicit analytical solution is better as it does not require knowledge of the steady state; this new solution is predictive as it only requires the dimensions of the domain and the initial distribution of the moles of the species in the reservoir. In the petroleum industry, this would serve as a vital tool to produce steady state composition of the fluids in the formation by just collecting samples from different parts of the reservoir. With the previous solution the fluids in the reservoir have to be at steady state for this tool to be used.
Figure 3-6: (a) Comparison of the steady state methane composition produced by numerical simulation using 21 grid-points (○) and the analytical solution (solid line). (b) A plot of the absolute deviation of the mole fraction calculated by the two methods.

Figure 3-7: Errors in equilibrium composition from the analytic solution against the number of grid points for methane/\textit{n}-decane mixture.
Figure 3-8: (a) Comparison of the steady state methane composition produced by numerical simulation using 121 grid-points (○) and the analytical solution (solid line). (b) Plot showing the absolute deviation of the mole fraction calculated by the two methods.

In the binary mixture we studied above, the steady state density difference was found to be approximately 8.0 kg.m\(^{-3}\) (as methane varies from 0.414 at the top to 0.386 at the bottom of the reservoir). This difference is small as it produces only 1.1\% variation in density across the reservoir. We thus test the validity of the new analytical solution in cases where the segregation is more pronounced at steady state.

Galliero and Montel (2008) developed a molecular dynamic (MD) algorithm to study the transient and the stationary (steady) state of gravity segregation in simple fluids. This approach was applied to Lennard-Jones mixtures composed of species that differ only by masses. They compared the results from the MD simulations to analytical solution obtained from thermodynamic modelling. This solution is similar to that used by previous authors (Eq. 3-22); it requires the knowledge of the steady state composition at a reference depth. As the molar volume was the same in these mixtures, the analytical solution is simplified:

\[
x^{(n)}_{i(z)} = \frac{(x^{(-L)}_{i(-L)}) \exp\left(\frac{g}{RT_{(-L)}}(M_x - M_i)(z + L)\right)}{1 + (x^{(-L)}_{i(-L)}) \exp\left(\frac{g}{RT_{(-L)}}(M_x - M_i)(z + L)\right)}
\]

In this section, we use our new analytical solution to compute the steady state of the LJ isotopes studied by Galliero and Montel (2008). We then compare the results to that from the MD simulations and the analytical solution presented in their work (Eq. 3-43). We simulated an isothermal binary equi-molar isotopic mixture of methane and super methane (the molecular weight is ten times that of methane) in a column of dimensionless thickness \(Z^* =\)
20 (approximately 7 nm), at the thermodynamic conditions of $T^* = 2.0$ and $\rho^* = 0.6$, where the former is the dimensionless temperature and the later is the dimensionless density of the LJ mixture (how this reduced parameters are calculated is described in Appendix A5). The methane LJ parameters used for this study are listed in table 3.2 (Cuadros et al., 1996), where $\sigma$, $\varepsilon$ and $k_B$ are the distance at which the LJ potential is equal to zero, the potential depth and Boltzmann constant, respectively.

<table>
<thead>
<tr>
<th>CH$_4$</th>
<th>$\sigma$ (nm)</th>
<th>$\varepsilon$ (J)</th>
<th>$\varepsilon/k_B$ (K)</th>
<th>$M$ (g mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.72</td>
<td>$1.96 \times 10^{-21}$</td>
<td>149.92</td>
<td>16</td>
</tr>
</tbody>
</table>

In order to test the limitations of our analytical solution, we subject the LJ mixture defined to various gravity potentials. The gravity acceleration $g^* = g\frac{\sum_{i=1}^{n} x_i M_i \sigma}{\varepsilon}$ has been varied from 0.02 to 0.32. As we expect, see Fig. 3-9, whatever $g^*$, the lightest component is enriched at the top of the column, and as the gravity amplitude is increased the segregation increases within the column. Results shown in Fig. 3-9, clearly indicate that MD simulations give a steady state composition profile in agreement with the thermodynamic model (Eq. 3.43). This is expected because, as mentioned earlier, the solution uses a reference composition from the MD simulation to calculate the other mole fraction values.

Comparing our new analytical solution to the MD simulation results for the different magnitudes, we observe that the derived expression works very well for all the cases, even when the steady state composition is an almost completely segregated ($g^* = 0.32$). Fig. 3-10, compares the absolute difference between the analytical solution and the MD simulation for all cases. We observe from this plot that the absolute differences are generally very small for the cases shown. The difference is negligible for lower gravitational potential $g^* = 0.02$, and as this potential increases the difference increases with a maximum average difference of 0.03 for the system with the highest gravity potential. This indicates that our new solution can predict the steady state compositional profile accurately even if the segregation is large.
It should be noted that the gravity values employed here are very large compared to those that occur in a petroleum reservoir. In fact, considering the binary LJ mixture and the configuration described previously, the corresponding ‘real’ column thickness under the normal acceleration due to gravity (9.81 ms\(^{-1}\)), vary from 270 (\(g^* = 0.01\)) to 8750 m (\(g^* = 0.32\)). These values are large compared to typical hydrocarbon reservoir heights which are generally in the range of 100 to 1000 m. This shows that the new analytical solution developed performs well even when there are large segregations at steady state.

Figure 3-9: Segregated steady state molar fraction profiles of the light component (\(x_1\)) in a binary equimolar isotopic mixture (\(M_2/M_1 = 10\)) at \(T^* = 2\) and \(\rho^* = 0.6\) under various gravity fields. The solid squares (■) indicates the results obtained from the MD simulations, the solid line the analytical solution proposed by Galliero and Montel (2008), Eq. 3-42 and the broken line represents results from the new analytical solution.
### 3.6 Results

Having validated both the numerical and new analytical solutions even for cases with non-linear segregated steady state composition profiles, we now use the computer program as a predictive tool. In this section, we shall use the numerical code to investigate the impact of thermal gradients and non-ideality of the fluid mixtures in the separation-mixing in 1D vertical system.

#### 3.6.1 Impact of Thermal Diffusion

Previous results have shown us that molecular and pressure diffusion always give a steady state profile with the lighter components of the fluids enriched at the top of the column, while heavier species migrate to the bottom. The other flux studied in this section; the thermal diffusion flux may enhance or weaken the separation produced by the previous fluxes depending on the thermal diffusion factor. In this section, we shall show the importance of modelling the thermal diffusion flux and the impact it has on the steady state profile.

In addition to an attempt to measure the thermo-diffusion factor in a ternary mixture composed of methane, n-butane and n-dodecane mixture, Touzet et al., (2011) also carried

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**Figure 3-10:** Comparison of the steady state composition of the light component produced by our new analytical solution and the MD simulations carried by Galliero and Montel (2008). This figure shows the comparison for different gravity fields; square (■): $g^* = 0.32$, triangle (∆): $g^* = 0.16$, circle (○): $g^* = 0.08$ and the crosses (ₓ): $g^* = 0.02$. 

---
out molecular dynamics simulations and micro gravity experiments to estimate the effect that thermal diffusion will have on the mixture compared to a system under the influence of gravity alone. They found that for this simple mixture, the two fluxes have opposite effects on the vertical distribution of the components in the fluid column. In this section we reproduce the results obtained by Touzet et al., (2011). We therefore carried out numerical simulations of both the isothermal and non-isothermal diffusion processes in a fluid column of height of 600 m with a ternary mixture composed of 20:40:40 of methane, n-butane and n-dodecane, respectively at an average temperature of 333.15 K and an isobaric pressure of 35 MPa using the thermal diffusion ratios obtained from their experiments (see Table. 3.3). The non-isothermal case has an imposed geothermal gradient of 3 K / 100 m.

Table 3-3: Parameters used for the numerical simulation for the methane/n-butane and n-dodecane mixture at 35 MPa and 333.15 K.

<table>
<thead>
<tr>
<th>Fluid Mixture Properties</th>
<th>Methane</th>
<th>n-butane</th>
<th>n-dodecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (kg.mol⁻¹)</td>
<td>16.04 × 10⁻³</td>
<td>58.10 × 10⁻³</td>
<td>1.70 × 10⁻¹</td>
</tr>
<tr>
<td>Molar volume (m³.mol⁻¹)</td>
<td>7.97 × 10⁻⁵</td>
<td>9.95 × 10⁻⁵</td>
<td>2.28 × 10⁻⁴</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>0.033</td>
<td>0.3507</td>
<td>5.112</td>
</tr>
<tr>
<td>Thermal diffusion ratio</td>
<td>-2.6</td>
<td>-1.6</td>
<td>4.2</td>
</tr>
</tbody>
</table>

Figure 3-11 shows the results of the numerical simulations for both the isothermal and non-isothermal segregation of the mixture. As we expected in the pure gravity segregation case, the lightest component, methane, is enriched at the top of the fluid column and n-dodecane accumulates at the bottom of the reservoir. However, when a geothermal gradient is introduced, the simulation results change significantly. The steady state compositional gradient of methane and n-dodecane are completely reversed because of the thermal diffusion effects. The heavier component, n-dodecane is now enriched at the top of the reservoir while methane migrates to the bottom of the column. This result demonstrates that for this ternary mixture the impact of thermal diffusion on the vertical distribution of the fluid components is much higher than that of the gravity segregation.

Another important point to note is that the steady state density variation is reversed when we introduce the thermal diffusion flux. In hydrocarbon reservoirs, the density usually increases with increasing depth. This is the case in the isothermal numerical simulation (see Fig. 3-12).
From a dynamic point of view, the inverted density profile (with a more dense fluid at the top of the reservoir) when a thermal gradient exists is unstable and would lead to a density driven convection process.

In order to validate our simulations, we compared our results with those produced by the molecular dynamics simulations of Touzet et al., (2011). Fig. 3-13 shows the absolute deviation between the two results. Results from these plots indicate that our numerical solution predicts the same behaviour observed in their work, as the deviation values are very small (to the third decimal place).

Figure 3-11: Mole-fraction profiles (methane: left figure, n-dodecene: right figure) for a ternary mixture of C₁-C₅-C₁₂ for isothermal case (■) and non-isothermal system (○).

Figure 3-12: Steady state density profile for the C₁-C₅-C₁₂ ternary mixture for both the isothermal (■) and non-isothermal (○) case.
Figure 3-13: Absolute difference between the steady state profiles produced by the numerical model and MD simulations by Touzet et al. (2011). Square (■): non-isothermal C₁, triangle (∆): non-isothermal C₁₂, circle (○): isothermal C₁₂ and the crosses (×): isothermal C₁.


Ratulowski et al., (2003) performed an experimental investigation into isothermal compositional grading in hydrocarbon reservoirs in order to understand the segregation observed in the Bull Winkle field. They hypothesized that composition gradient was a result of gravity. They designed a special centrifuge system capable of producing a potential difference across a live oil column equivalent to 304.8 m (1000 ft). In order to test their apparatus, experiments were initially carried out on a ternary mixture of methane, n-pentane and methylnaphthalene. They chose this mixture based on work by Schulte (1980), who observed that the oils containing at least one aromatic component graded more than oils that contain just saturated hydrocarbons.

In this section, we aim to reproduce the experimental results obtained by Ratulowski et al., (2003) and highlight the importance of accurately modelling the non-ideality of mixtures. We shall also analyze the cross diffusion effect that occurs in the mixing of the methane/ n-pentane and methylnaphthalene mixture and see if this has any effect on the timescale of the mixing process.
Table 3-4: Parameters used to model the fluids in Ratulowski et al., (2003) centrifuge experiment obtained from REFPROP 8.0 (Lemmon et al., 2007).

<table>
<thead>
<tr>
<th>Fluid Mixture Properties</th>
<th>Methane</th>
<th>n-pentane</th>
<th>Methylnaphthalene</th>
<th>Undecane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (kg.mol⁻¹)</td>
<td>16.04 × 10⁻³</td>
<td>72.15 × 10⁻³</td>
<td>142.2 × 10⁻³</td>
<td>156.3 × 10⁻³</td>
</tr>
<tr>
<td>Molar volume (m³.mol⁻¹)</td>
<td>0.597 × 10⁻⁴</td>
<td>1.08 × 10⁻⁴</td>
<td>1.36 × 10⁻⁴</td>
<td>2.15 × 10⁻⁴</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>0.033</td>
<td>0.3507</td>
<td>5.112</td>
<td>0.957</td>
</tr>
</tbody>
</table>

To compare the results we obtained from our simulations to the experimental results, we have to relate the potential in the rotating centrifuge to that of a gravitational column. For equivalent grading, the rotational speed is related to the acceleration due to gravity by (Ratulowski et al., 2003):

\[
g(h) = \frac{\omega^2}{2} \left( r^2 - r_0^2 \right)
\]

where \( h \) is the height of the oil column, \( \omega \) is the rotational speed (rad s⁻¹), \( r \) the distance from the axis of rotation and \( r_0 \) is the distance from the near end of the centrifuge to the to the axis of rotation. The vessel dimensions have been converted to reservoir height using Eq. 3-43 so that we can compare the results directly with our numerical simulations. For the geometry of the experiment, Ratulowski applied a rotational speed of 5,000 rpm to achieve a gravity potential for a column with thickness of 304.8 m. The experiments were performed at a temperature and pressure of 295 K and 46 MPa respectively. The authors found that the maximum grading of the ternary mixture occurs when with the initial composition was set to: 52.5 mole methane, 27.9 mole n-pentane and 19.6 mole methylnaphthalene. Ting et al., (2009) tried to reproduce the steady state composition gradient for the ternary system of C1-nC5-MNP using centrifugal experiments similar to that of Ratulowski et al., (2003) and numerical grading model based on Gibbs law of sedimentation. From analyzing the results obtained from their work, we observed that the numerical model generated did not quantitatively match the results obtained from the experiments.
To predict the results obtained from the experiments we initialize our 1D domain with uniform mole fractions (case 1) of methane, $n$-pentane and methylnaphthalene (MNP) of 0.525, 0.279 and 0.196, respectively. We model the mixture using Peng-Robinson EOS to account for the non-ideality of the fluid. Figure 3-14 shows a comparison between the numerical simulation results and those obtained from the centrifugal experiments by Ratulowski et al., (2003). In both cases the pentane composition in the domain is almost constant across the column, while the methane and MNP segregate to give a methane rich fluid at the top of the reservoir and MNP rich fluid at the bottom of the reservoir. The steady state distribution observed in Figure 3-14 shows that the segregation in the experimental results is greater than that produced from the numerical solution (this is more visually noticeable in the methane and MNP steady state profiles). This however is exaggerated due to the scale of the plot, thus it is important to quantify the differences between the two cases. Fig. 3-14 shows the absolute deviation between the two results. The maximum deviation between the experiment and numerical solution on the three plots always occurs at the top or the bottom of the reservoir, where the separation is at its maximum. The maximum absolute value of the deviation for methane, $n$-pentane and MNP calculated from the plots are 5%, 4% and 15%, respectively, while the average absolute values of the deviations for methane, pentane and MNP are 2%, 2% and 6%, respectively.

As we mentioned earlier, the most important parameter in the gravity and molecular diffusion process is the thermodynamic factor. The deviations observed between the simulations and experiments may arise due to the EOS (Peng-Robinson) used to calculate this parameter. Also the experiments were initially plagued with a few problems such as leakages and mercury contamination. These faults were fixed in subsequent runs. Uncertainties in the spin times and sampling of the fluids however remained throughout the experiments. Considering all of these factors the agreement between the experiment and numerical solutions is acceptable.
Figure 3-14: Comparison of the results from the numerical model to the experimental results obtained by Ratulowski et al., (2003) for the methane/pentane/MNP mixture. The activity coefficient were found using Peng-Robinson EOS in this numerical solution. The solid black line represents the numerical solution while the diamonds (◊) represent the experimental results.

Figure 3-15: Difference between the steady state compositions between the numerical solution and the experiments by Ratulowski et al., (2003). Square (■): Methane, (△):MNP, circle (○):n-pentane.

Ratulowski et al., (2003) also made a comparison between the fluid mixture used in the experiment described above and a mixture of methane, n-pentane and n-undecane. They
modelled both fluids using a modified Redlich-Kwong EOS in Shell’s proprietary phase-behaviour package. They observed that even though the heaviest components of the two ternary mixtures have similar molecular weights that the mixture containing an aromatic species graded more. They found that the segregation in the methane mole-fraction in the methane/n-pentane/MNP mixture reservoir was approximately 5.5 times than that of a same composition mixture of methane/n-pentane/n-undecane (see Fig. 3-16). To investigate this phenomenon, we simulate both mixtures with initial composition of 0.5, 0.3 and 0.2 as ideal, and then as real mixtures using first the Peng-Robinson EOS and then the UNIFAC-Dortmund EOS (Gmehling et al., 2002). We did this to highlight the importance of the EOS used to calculate the activity coefficients. We used correlations by Nishiumi et al., (1998) and Gao et al., (1992) to empirically determine the binary interactive parameters for the alkane-aromatic and alkane-alkane combination, respectively. The elements of the thermodynamic factor calculated from the two equations of states are shown in Figure 3.17. The results are plotted as a function of changing mole fraction of pentane; the methane composition was kept constant at 0.5 throughout. For both mixtures, the two equations of state gave different values of the thermodynamic factor.

![Figure 3-16: Predicted steady state ethane mole composition for a 50:30:20 methane/n-pentane/MNP and methane/n-pentane/n-undecane systems (Ratulowski et al., 2003).](image)

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Figure 3-17: Elements of the Thermodynamic factor matrix for the two ternary mixtures.

Figure 3-18 shows the predicted methane steady state compositions obtained from our numerical simulation of the two mixtures assuming ideality and also the non-ideal cases where the thermodynamic factors are calculated using the Peng-Robinson EOS and the UNIFAC-Dortmund EOS.
Figure 3-18: Comparison between the separation of methane in the methane/\textit{n}-pentane/undecane and methane/\textit{n}-pentane/MNP mixtures for both ideal and real cases.

From Figure 3-18(c), the steady state separation of methane in the domain when the two mixtures are modelled as ideal is 0.011 and 0.014 in the \textit{n}-undecane and MNP mixture, respectively. Comparing the two values, we notice that the change in methane mole fraction within the MNP mixture is a factor of 1.3 more than that in the \textit{n}-undecane. This ratio is similar to that of the ratio of the densities of the two components; the density of \textit{n}-undecane and MNP are 726 kg.m\textsuperscript{-3} and 1043 kg.m\textsuperscript{-3} (approximately 1.4 times of the former). The separation is thus governed by density difference in the ideal systems as we expect from Eq. (3.31). For the non-ideal system we tested the predictions from the two EOS. In Fig. 3-18(b), we
observe, using the PR-EOS, a higher segregation of methane of 0.023 for the MNP system. The inclusion of non-ideality had negligible effect for the n-undecane mixture (methane separation at steady state is 0.012). When the UNIFAC-Dortmund EOS was used to calculate the activity coefficient, the separation of methane in the MNP mixture increased compared to the ideal mixture (0.017), while the methane separation in the n-undecane mixture decreased to 0.008, as illustrated in Fig. 3-18 (b)

![Graphs showing segregation of methane in different mixtures](image)

Figure 3-19: Elements of the inverse of the thermodynamic factor matrix for the methane/n-pentane/MNP and methane/n-pentane/undecane mixtures.

The segregation obtained from the numerical simulation for each case can be explained using the explicit analytical solution we derived earlier to quantify the separation in ideal and real mixtures under the influence of gravity and molecular diffusion (Eq. 3-31 and Eq. 3-35).
Table 3.5 and 3.6 show the values of \( \sum_{j=1}^{n-1} (\Gamma_{ij}^{-1} \theta_j) \) for methane and \( n \)-pentane for all three cases for varying compositions of \( n \)-pentane (\( 2Lx_1^0 \) is the common factor in the solution for steady state separation for ideal and real mixtures, we thus ignore this parameter). For an ideal system, the inverse of the thermodynamic factor \( \Gamma_{ij}^{-1} \) is an identity matrix; therefore the separation term would only have diagonal elements. Thus the \( \sum_{j=1}^{n-1} (\Gamma_{ij}^{-1} \theta_j) \) for an ideal system in the tables for the species \( i \) is equivalent to \( \theta_i \).

Table 3-5: Methane and \( n \)-pentane \( \sum_{j=1}^{n-1} (\Gamma_{ij}^{-1} \theta_j) \) calculated by the analytic solution for the methane/\( n \)-pentane/MNP mixture

<table>
<thead>
<tr>
<th>x nC(_5)</th>
<th>methane</th>
<th>n-pentane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ideal</td>
<td>PR-EOS</td>
</tr>
<tr>
<td>0.10</td>
<td>9.10</td>
<td>12.51</td>
</tr>
<tr>
<td>0.20</td>
<td>9.10</td>
<td>13.76</td>
</tr>
<tr>
<td><strong>0.30</strong></td>
<td>9.10</td>
<td><strong>15.08</strong></td>
</tr>
<tr>
<td>0.40</td>
<td>9.10</td>
<td>15.67</td>
</tr>
<tr>
<td>0.50</td>
<td>9.10</td>
<td>14.45</td>
</tr>
</tbody>
</table>

Table 3-6: Methane and \( n \)-pentane \( \sum_{j=1}^{n-1} (\Gamma_{ij}^{-1} \theta_j) \) calculated by the analytic solution for the methane/\( n \)-pentane/undecane mixture

<table>
<thead>
<tr>
<th>x nC(_5)</th>
<th>methane</th>
<th>n-pentane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ideal</td>
<td>PR-EOS</td>
</tr>
<tr>
<td>0.10</td>
<td>7.41</td>
<td>7.75</td>
</tr>
<tr>
<td>0.20</td>
<td>7.41</td>
<td>7.74</td>
</tr>
<tr>
<td><strong>0.30</strong></td>
<td><strong>7.41</strong></td>
<td><strong>7.79</strong></td>
</tr>
<tr>
<td>0.40</td>
<td>7.41</td>
<td>7.99</td>
</tr>
<tr>
<td>0.50</td>
<td>7.41</td>
<td>8.77</td>
</tr>
</tbody>
</table>
The increase in the segregation of methane when the methane/n-pentane/MNP mixture is modelled as non-ideal can be explained by the reference to Table 3.5. For this mixture $\theta_1 \approx 9 \times 10^{-5}$ and $\theta_2 \approx -8 \times 10^{-6}$. The product $\Gamma_{22}^{-1} \theta_2$ gives a negligible value (for the both EOS, $\Gamma_{22}^{-1}$ is positive and $0 < \Gamma_{22}^{-1} < 1$). The segregation for the real mixtures can thus be approximated by the product $\Gamma_{11}^{-1} \theta_1$. The increase in the separation is thus due to the magnitude of $\Gamma_{11}^{-1}$, and as we can notice in Fig. 3-19, this is greater than one for the two EOS. Thus the segregation would always be greater in the mixtures modelled as real compared to the ideal case; $\Gamma_{11}^{-1} \theta_1 > \theta_1$.

Table 3.6 suggests that there will be negligible difference in the separation of methane in the methane/n-pentane/ n-undecane mixture when modelled as an ideal fluid and when the fluid is modelled as real using the Peng-Robinson EOS. We observe the same trend in our numerical simulation. This occurs because the off diagonal term of the inverse of the thermodynamic factor $\Gamma_{12}^{-1}$ are very small. Thus the product $\Gamma_{12}^{-1} \theta_2$ is negligible compared to $\Gamma_{11}^{-1} \theta_1$. From Figure 3-19, we observe that the diagonal term $\Gamma_{11}^{-1}$ is also approximately one (similar to that of an ideal mixture). The separation term for the methane in this mixture modelled by the Peng-Robinson EOS is thus similar to that of an ideal mixture $\theta_1$. The change in the separation of this component observed when the non-ideality of the fluid is modelled using the UNIFAC Dortmund as the diagonal term is not close to one and the off diagonal term is big enough to play part in the segregation of this component.

Next, we compared the ratios of separation from our simulations to those reported by Ratulowski et al., (2003). We observe that our non-ideal models predict an increased segregation in the MNP mixtures. However, the ratio of separation found in our models; approximately 2.1 for both cases are far lower than the factor of 5.5 found in their work. Previous work by Besong (2010) calculated the separation of these two mixtures but no agreement was observed. This is because the previous models did not consider the modelling of the activity coefficients; the mixtures were treated as ideal fluids. Our model out performs previous ones as we consider the non-ideality of the fluid. However, we do not obtain a perfect match as they used another EOS (Redlich-Kwong) in their study to model the non-ideal mixing of the fluid.
Another interesting characteristic we noticed in Table 3.5 during our analysis was that the \( \sum_{j=1}^{n-1} (\Gamma_{ij}^{-1} \theta_j) \) for the intermediate component (n-pentane) changes sign between the ideal and non-ideal mixture for methane, n-pentane and MNP mixture. In the ideal system, n-pentane is enriched at the bottom of the reservoir while this is reversed in the systems where the fluid is modelled as a non-ideal mixture (see Fig. 3-20). This can also be explained by examining the elements of the inverse of the thermodynamic factors and the \( \theta_i \) terms used to approximate the separation. For ideal systems the off diagonal terms of the inverse thermodynamic factor matrix is zero hence the product \( \Gamma_{21}^{-1} \theta_1 \) is also zero. Thus the \( \sum_{j=1}^{n-1} (\Gamma_{ij}^{-1} \theta_j) \) term which infers separation shown in Table 3.5 is defined by just \( \theta_2 \), which is negative. For the real (non-ideal) systems, the non-diagonal terms are not zero and \( \theta_1 \) (the gravity diffusion driving force for methane) is large and positive. This would lead to the separation changing direction as \( \Gamma_{21}^{-1} \theta_1 > \Gamma_{22}^{-1} \theta_2 \). We notice that the mixture modelled by UNIFAC Dortmund showed an increased segregation compared to that modelled using PR-EOS. In this study, we used the correlation by Gao et al., (1992) and Nishiumi and Arai (1988) to calculate the binary interactive parameters required for the PR-EOS for the alkanes and alkane-aromatic systems, respectively. We attribute this to the increase in \( \Gamma_{21}^{-1} \) term (see Fig. 3-19) that leads to large differences between \( \Gamma_{21}^{-1} \theta_1 \gg \Gamma_{22}^{-1} \theta_2 \).

![C1/C5/MNP](image)

Figure 3-20: n-pentane steady state compositional profile produced by the numerical solution for both ideal and real cases of the methane/n-pentane/MNP mixture.
This exercise highlights the importance of correctly modelling the non-ideality of the mixtures as modelling these mixtures as ideal would give wrong steady state solutions for the methane/n-pentane/MNP and methane/n-pentane/undecane mixtures.

### 3.6.3 Reverse Diffusion and its Impact on Steady State Timescales

#### 3.6.3.1 Study of the Transient n-pentane composition profile

Whilst investigating the differences in the segregation of n-pentane in the ideal and real systems for the methane, n-pentane and MNP mixture, we also observed that the model for ideal mixtures reached steady state in half the time taken for the real mixtures to reach steady state. The ideal mixture reaches equilibrium at 240,000 years while when non-ideality is introduced the UNIFAC Dortmund and Peng-Robinson Model reach steady state at 400,000 years and 320,000 years, respectively. This suggests that the non-ideality of the mixture also affects the timescale of the mixing process.

![Diagram](Figure_3-21.png)

**Figure 3-21:** Change in n-pentane composition with time for methane/n-pentane/MNP mixture for both Ideal and real systems for $z = -117.6$ m.

To illustrate this, we have plotted the change in the composition of n-pentane with time until steady state is attained for 5th grid-point (in Fig. 3-21, we plot the grid-point $z = -117.6$ m for a reservoir, $-L \leq z \leq L$). We defined that the steady state is reached when the percentage change in mole fraction is less than $10^{-6}$ between two successive iterations at each grid point. When the ternary mixture is assumed to be ideal, it can be seen that the n-pentane composition initially increases then reduces to a steady state composition greater than the initial composition. However in the real cases, the composition also initially increases but then decreases to a composition less than its initial composition before steady state is
attained. The effect is more pronounced when the real mixture is modelled using UNIFAC-Dortmund EOS.

If we investigate the transient compositional profiles of \( n \)-pentane (Fig. 3-22) for a real system (modelled by the UNIFAC Dortmund EOS) further, we notice that the composition at the grid points near the boundaries initially segregate in a certain direction, then the mixing is reversed. This is evident as “humps” in Figure 3-22, which shows the compositional profile of \( n \)-pentane from the 3\(^{\text{rd}}\) to the 12\(^{\text{th}}\) iterations. It should be noted that using the stability criterion (Eq.3-15), the time-step size for this system was found to be 74 years; therefore the 12\(^{\text{th}}\) iteration in figure 3-22 corresponds to 819 years.

![Figure 3-22: Transient \( n \)-pentane composition profile for the methane/\( n \)-pentane/MNP mixture, where the thermodynamic factor is computed using UNIFAC-Dortmund for the first few time-steps.](image)

This behaviour can be explained by examining how the \( n \)-pentane composition changes over time for two adjacent grid points (\( z \) and \( z+1 \)). In Figure 3-23, we plot the \( n \)-pentane composition against number of time-step for the points \( z = -117.6 \) m and \( z = -101.6 \) m, the former being lower in height than the later in our grid orientation. We notice that the \( n \)-pentane composition is initially higher in the lower grid point, and then after 8880 years the curve representing \( n \)-pentane composition in the higher grid point intersects that of the lower grid point. After this the \( n \)-pentane composition is then higher in the higher grid-point for the remainder of the simulation.
This behaviour can be observed better if we plot the change of the compositional gradient with time as the simulation reaches steady state. Figure 3-24, shows how a plot of the \( n \)-pentane compositional gradient against number of iterations for grid point \( z = -117.6 \) m. We notice that the \( n \)-pentane compositional gradient is negative until about 4700 years for the system modeled using UNIFAC Dortmund (see Fig. 3-24(a)). Recall that the compositional gradient is the driving force for the molecular diffusion process. The change in the sign of the gradient implies that \( n \)-pentane would diffuse in a different direction after the 4700 years. This behaviour may be due to the phenomenon introduced in the earlier chapter as reverse diffusion. This behaviour is also observed in the ternary mixture where the thermodynamic factors are modelled by Peng-Robinson EOS after 530rd time-step. The reversal occurs at a
much later time of 68,000 years as the time-step size for Peng Robinson simulation (129 years) is larger than that of the UNIFAC-Dortmund simulation (74 years). This phenomenon observed in the real mixture simulation does not occur in the simulation for ideal mixture as the compositional gradients is always negative (Fig. 3-24 (b)), thus the species diffuses towards the bottom of the reservoir throughout the simulation.

![Diagram](image)

**Figure 3-24:** Change of n-pentane compositional gradient with time for both the real and ideal cases for the methane/n-pentane/MNP mixture for $z = -117.6$ m.

The reader is reminded that we use a central difference method to calculate the composition difference in this work to calculate this parameter more accurately, thus time step at which reverse diffusion occurs in Fig.3-24 differs from that found in Fig.3-23.

### 3.6.3.2 Diffusion Interactive effects in the C1/C5/MNP mixture

In order to confirm the reverse diffusion signature we plot the molecular diffusion flux for species $i, j_i^M$ against the compositional gradient $-\partial x_i/\partial z$ for methane and n-pentane for both the ideal and real mixture systems for the grid point $z = -117.6$ m (Fig. 3-25) for all the time-steps until steady state is attained. This plot is similar to the plot (Fig. 2-1) modified from Taylor and Krishna (1993) in the previous chapter (Fig. 2-1). If the sign convention of the x-axis value and the y-axis value of this plot are the same the component diffuses normally i.e. diffusion of the component is in the direction predicted by its composition gradient. In the cases where this is not the case (as we can see in our real mixture models), the component
diffuses in an opposite direction predicted by its gradient due to interaction effects in multi-component diffusion.

If we analyze figure 3-25, we notice that in the ideal mixture case the methane and n-pentane always diffuse normally i.e. in the direction predicted by their mole-fraction gradient. Methane continually segregates to the top of the reservoir while n-pentane continues to be enriched at the bottom. In the real mixtures, methane also diffuses normally to the top of the reservoir. However, the n-pentane in both real mixtures starts diffusing normally and after a certain time we encounter a reverse diffusion phenomena (a negative value of $-\partial x_{nCS}/\partial z$ has a corresponding positive value of $J^M_{nCS}$). We observe that for the grid point $z = -117.6$ m, the reverse diffusion starts to occur in the mixture modelled using the UNIFAC-Dortmund EOS at the 67th time step. This same characteristic is seen in the simulations carried out for the mixture modelled by PR-EOS, but this happens at a later time step of 530 for $z = -117.6$ m, as we already seen in Fig. 3-24. This confirms that reverse diffusion is the phenomenon that leads to the ‘humps’ observed in Fig. 3-22 and the behaviour illustrated in Fig. 3-21, where n-pentane diffuses to a steady state mole-fraction lower than its initial value even though the composition of this species initially increases.

This trend occurs at every grid point in the model at different times; thus leading to the ‘humps’ seen in Fig. 3-22 at different times for each grid-point. The grid point analyzed here $z = -117.6$ m is in the lower part of the reservoir, thus the results explained above show that n-pentane initially diffuses to the lower part of the reservoir then after a certain time when the reverse diffusion phenomena kicks in the n-pentane is enriched at the top of the reservoir. The reverse diffusion phenomenon also leads to longer timescales for the ternary mixture to attain steady state compared to ideal mixture.
Figure 3.25: Molecular diffusion flux versus compositional gradient for the methane/n-pentane/MNP mixture for the real (a. UNIFAC-Dortmund, b.Peng-Robinson EOS) and the ideal systems. Solid line: n-pentane and broken line: methane.
3.7 Chapter Summary

We have investigated the impact of diffusion (molecular, pressure and thermal) processes on vertical steady state compositional gradients in the subsurface for both isothermal and non-isothermal cases. We have developed a numerical model to solve the diffusion equations explicitly and also have presented a new analytical solution to predict the steady state segregation for a system under the influence of gravity segregation alone. The new developed analytical solution performs well and gives very consistent results when compared to the numerical simulation even when the density difference in the system is not negligible (although one of the main assumptions made when deriving this solution was that the density difference is relatively small).

We also investigated the importance of modelling thermal diffusion, as previous work has usually omitted this flux when studying the impact of diffusion on vertical compositional grading. In the system we studied we showed that the thermal diffusion can reverse the segregation process, leading to heavy components being enriched at the top of the reservoir and vice versa (opposite signature of gravity segregation).

In the last section, we revisited the experiments performed by Ratulowski et al., (2003) on a ternary mixture of methane, pentane and methylnaphthalene using our numerical model. We found out that the activity coefficient is one of the most important parameters that govern the non-ideal mixing by molecular and pressure diffusion. Our numerical results matched the experimental findings reasonably well. This discrepancy is attributed to uncertainties in the centrifugal spin time and the sampling of the fluids used in the experiments.

Finally, we analyzed the transient behaviour of this mixture and observed that in the intermediate component (n-pentane in our mixture) undergoes reverse diffusion. This results in the non-ideal mixtures taking longer to attain steady state (almost double that of the ideal counterpart) and having a different segregation to that observed for the ideal mixtures.
Chapter 4

Natural Convection and Molecular Diffusion in a 2D Domain

In two (2D) or three dimensional (3D) domains fluid mixing is, in addition to the diffusional processes, affected by natural convection, due to density gradients caused by composition or thermal gradients. Previous works by several authors (England et al., (1995 and 1987), and Smalley and Muggeridge (2010) to a name a few), and order of magnitude estimates for equilibrium timescales show that natural convection takes place at a faster rate than the diffusion processes. It is thus important to model natural convection alongside diffusion as the presence of natural convection could have a large impact on reducing the steady state timescales. Ratulowski et al., (2003) demonstrated the reduction in timescales in centrifuge experiments to induce gravitational potential across a live oil column of 1000 ft. In their work, they pointed out the importance of spinning the pressure vessel at an angle (in order to induce convection), rather than letting it spin horizontally where molecular diffusion would be the only dominant flux. They found out that this greatly reduces the time needed to achieve equilibrium.

In this chapter, we present the equations that govern the transient segregation-mixing process in a 2D reservoir under the influence of molecular diffusion and natural convection for single phase mixtures. Then we compare the numerical solution obtained with the reservoir simulation package CMG STARS® using available analytical solutions for simple cases. The
impact of different reservoir parameters and configurations on the equilibrium timescale is then studied.

4.1 Governing Equations

The unsteady state equations for the bulk and species mass conservation are given by the equations below:

\[
\frac{\partial c}{\partial t} + \nabla (cV) + \sum_i q_i = 0, \tag{4-1}
\]

\[
\frac{\partial (cx_i)}{\partial t} + \nabla(cx_iV) + \nabla j_i + q_i = 0, \quad i = 1, \ldots, n - 1, \tag{4-2}
\]

where \( t, c, V, j_i \) are the time, total molar concentration, the mass average Darcy velocity and total diffusion flux (non-convective) of component \( i \). In this work, there is no flow into and out of the reservoir from an external source (no sources or sinks). The species molar production rate per unit volume term \( q_i \) is thus set to zero. The diffusion term for component \( i \) is expanded as:

\[
j_i = -c \left( \sum_{j=1}^{n-1} D_{ij}^x \nabla x_j + D_i^p \nabla P + D_i^T \nabla T \right), \quad i = 1, \ldots, n - 1 \tag{4-3}
\]

taking into account molecular diffusion, pressure diffusion and thermal diffusion associated with the movement of fluid molecules due to gradients in concentration, pressure and temperature.

\( D_{ij}^x, D_i^p \) and \( D_i^T \) are the coefficients of molecular, pressure and thermal diffusion, respectively. The diffusive flux results from deviation of the velocity of component \( i \) from the velocity of the bulk fluid. It should be noted that in the above equations only \( n-1 \) terms are independent, thus we can only calculate the \( n^{th} \) term if we know the other terms. For example, due to the restriction that the diffusive flux terms for all components \( i \) add up to zero, the \( n^{th} \) term is given by:
The reader is reminded that in general that the respective diffusivity is a matrix:

\[
D_{ij}^x \equiv [D_{ij}^x], \quad i, j = 1, \ldots, n - 1,
\]

\[
D_i^p \equiv [D_i^p], \quad i = 1, \ldots, n - 1,
\]

\[
D_i^T \equiv [D_i^T], \quad i = 1, \ldots, n - 1
\]

In this chapter, we shall only be dealing with the impact of molecular diffusion and convection on two component mixtures; the molecular diffusion coefficient matrix thus becomes a scalar. Therefore, the equation for the total diffusive flux (Eq. 4.3) becomes:

\[
J_i = -c \left( \sum_{j=1}^{n-1} D_{ij}^x \nabla x_j \right), \quad i = 1, \ldots, n - 1
\]

### 4.1.1 Reservoir Geometry

We will be considering a two dimensional porous medium with width \( b \) and a height \( h \) (Figure 4-1) saturated with a single-phase mixture of \( n \) components.

![Figure 4-1: Geometry and boundary conditions for the 2D domain.](image-url)
Similar to the previous chapter, the cross section of the reservoir is assumed to be bounded by impervious rock, thus the total flux for all components vanishes at the boundaries. The boundary conditions for Eqs. 4-1 and 4-2 are:

\[ j_i \cdot \mathbf{n} = 0, \quad i = 1, \ldots, n - 1, \quad x = 0, b, \quad \text{and} \quad z = 0, h, \quad \text{4-7} \]
\[ v \cdot \mathbf{n} = 0, \quad x = 0, b, \quad \text{and} \quad z = 0, h \quad \text{4-8} \]

where \( \mathbf{n} \) is the unit vector. These boundary conditions imply:

\[ \sum_{j=1}^{n-1} D_{ij}^X \frac{\partial x_j}{\partial x}, \text{and} \quad v_x = 0, \quad x = 0, b, \quad \text{4-9} \]
\[ \sum_{j=1}^{n-1} D_{ij}^Z \frac{\partial x_j}{\partial z} = 0, \text{and} \quad v_z = 0, \quad z = 0, h. \quad \text{4-10} \]

Using the Darcy equation (Eq. 2-19), we obtain the boundary conditions required for the integration of the pressure equation:

\[ \frac{\partial P}{\partial x} = 0, \quad x = 0, b, \quad \text{4-11} \]
\[ \frac{\partial P}{\partial z} = -g \frac{\partial \rho}{\partial z}, \quad z = 0, h. \quad \text{4-12} \]

We initialize the domain by specifying the temperature and composition distribution of each species. We specify a reference pressure and perform vertical equilibrium calculations based on the fluid density and reservoir thickness to initialize the pressure in the domain. We are interested mainly in how convection and diffusion affects fluid mixing since reservoir filling, thus we initialize the system as though it has inherited the compositional gradient due to reservoir filling. The domain is filled with a denser mixture in the right hand side while a less dense fluid occupies the left hand side to represent reservoir being charged from the left hand side.
4.1.2 Temperature Profile

We also investigated the impact of thermal gradients on the natural convection process. In this case, we assumed the reservoir is bounded by an impervious rock that has constant temperature gradients in both horizontal and vertical directions (similar to that used by Riley and Firoozabadi; 1998). The temperature field is assumed to be a linear function of $x$ and $z$: 

$$T = T_x x + T_z z + a,$$

where $T_x$, $T_z$ and $a$ are the horizontal temperature gradient, vertical temperature gradient and a constant. If we set the temperature at $x = x_0$ and $z = z_0$ equal to $T_0$, then:

$$T = T_x (x - x_0) + T_z (z - z_0) + T_0,$$

where $x_0$ and $z_0$ are the coordinates of the reference point. The reference point in this work is chosen as the first node in the domain; $n(i = 1, k = 1)$.

4.1.3 Reservoir Simulator: CMG STARS®

We use the reservoir simulation package STARS® by CMG to solve the above numerical problem in the 2D domain. STARS® is an industry standard thermal reservoir simulator. STARS® model is based on a finite difference numerical simulation and can be used to model the fluid mixing process. The software was chosen because it is one of the few reservoir simulation packages that can model molecular diffusion and thermal effects.

This software was developed to model the thermal and chemical recovery processes in hydrocarbon reservoirs on a production timescale. Thus simulations are limited to a 5 million years timescale. Reservoir fluid mixing prior to production takes place on geological timescales which might be higher than 5 million years. To deal with this problem, when steady state in the system does not occur within 5 million years, we initialize the model using the results (compositions) from the previous run till equilibrium state is achieved\(^1\).

We use CMG PVT Tool, WINPROP to calculate the fluid properties for the STARS® simulations. WINPROP calculates the densities of the pure components of the fluids using

---

\(^1\) This was achieved by using the *INIT_FROM_RESTART key word on CMG STARS®.
\(^2\) Confidential presentation of Hongjun of BP, Exploration & Production Technology
the Peng-Robinson equation of state, while the mixture density is computed assuming ideal mixing,

$$\frac{1}{\rho} = \sum_{i=1}^{n} \frac{x_i}{\rho_i}$$  \hspace{1cm} 4-14

The viscosities of the species are calculated using the correlation proposed by Lohrentz et al. (1964).

STARS uses the implicit pressure-explicit saturation (IMPES) method as a default technique to solve for the solution of the reservoir problem. Therefore, we had to make sure we do not choose a maximum time-step that leads to an unstable solution. At the same time, we made sure the time-step was not too small that the simulation time was excessive. We scaled the maximum time-step when the grid was refined or permeability was changed.

4.2 Quantifying Fluid mixing

In order to quantify the influence of convection (thermal and/or gravity driven) and molecular diffusion on the 2D rectangular cross section system easily, we use certain quantitative indicators (metrics) to better represent the impact of these fluxes on the different fluids and reservoirs over time.

4.2.1 Composition Separation and Density Gradient

To quantify the diffusional fluid mixing process we use the separation metrics, which is the difference in the species mole fractions from the two extremes of the domain. We also use the average mass density gradient across the reservoir (both lateral and vertical) to illustrate the fluid motion. These two terms are calculated using:

$$S_i = x_{i(0,0)} - x_{i(n,n)}$$  \hspace{1cm} 4-15

where subscript $n$ represents the last nodes for the 2D domain and

$$D_z = \frac{(\bar{\rho}_{\text{top}} - \bar{\rho}_{\text{bottom}})}{H}$$  \hspace{1cm} 4-16
where $D_z$ and $D_x$ are the vertical and lateral density gradients, respectively.

### 4.2.2 Rayleigh Number

In cases where convection is caused by thermal gradients, we use the Rayleigh-Bernand number to describe the extent of thermal convection. This dimensionless number is defined in section 2.3.1 as the ratio of the buoyancy forces to the heat transfer. This term is used to investigate whether thermal convection is active in the reservoir. The Rayleigh number is calculated using equation 2.20 using average values of the fluid properties such as the permeability, fluid viscosity, heat capacity and density. The temperature difference is calculated using the vertical or lateral temperature difference.

### 4.3 Software/ Model Validation

We have selected a set of analytical solutions to validate the mixing process (due to convection and molecular diffusion) modelled by CMG STARS®. For this purpose, we compare the results of the model for convective mixing with the analytical solution proposed by Gardner et al., (1962). We also test the validity of the molecular diffusion mixing with the analytical solution derived by Crank (1975).

#### 4.3.1 Validation of Convection Mixing Time

Gardner et al., (1962) presented *semi-analytical* solutions based on experiments for the motion of the interface between two miscible fluids with a density difference in a rectangular cross-section as a function of time. There is no bulk flow through the models discussed in their work and convection currents are initiated solely due to the density difference in the domain. This analysis is appropriate to the problem of density driven mixing on a geological timescale. They provided solutions for horizontal, vertical and inclined reservoir configurations. England et al., (1995) compared the semi-analytic solution to numerical
solutions and showed good agreement. In this section, we shall present the analytical solutions and then use these to validate the gravitational overturning simulations carried out on CMG STARS®.

In this study we used a horizontal rectangular model (where the lateral distance is larger than the vertical distance) initialized with the heavy and light fluids separated by a vertical interface parallel to the y-z plane. This initial condition with a lateral density difference is analogous to the natural reservoir charging behaviour; where the source rocks initially fills the reservoir with heavier fluids, then as the source rocks matures it release lighter fluids (then gases). As time progresses the gravitational overturning process occurs as the denser fluid migrates to the bottom of the domain and the light fluid moves to the top. The interface between the fluids becomes tilted and gradually moves to steady state condition (horizontal). This movement is described by the parameter $(2x/h)$, which increases from zero as the interface moves towards the horizontal (see Fig. 4-3).

For simplicity, Gardner et al., (1962) assume the interface is a plane surface at all times. Their experimental studies have backed this assumption. As long as the viscosity ratio in the model is relatively small (approximately equal to 1) the interface would remain planar. At higher viscosity ratios the motion becomes complicated because of the non linear dependency of viscosity on composition of the mixture and the interface would also become significantly curved. For all the cases shown in this section, the viscosity ratio is set to equal to one.

![Figure 4-2: Initial condition for density driven convection process at t = 0 for analytical solution for Gardner et al., (1962).](image)

Three stages of the motion of the interface are considered in the work by Gardner et al., (1962): tilting at the early, intermediate and late times (near steady state). In the early stages of motion, the projection of the interface on the base of the domain is given by:
Here $h$ is the height of the reservoir, $K_h$ and $K_v$ are the horizontal and vertical permeabilities respectively; $\phi$, $t$, $\bar{\mu}$ and $\Delta \rho$ represent the porosity, time, the average viscosity and density difference between the two fluids.

At late times, when the interface broadens and becomes long, the length of the interface increases at a slower rate which is directly proportional to the square root of the time:

$$\left(\frac{2x}{h}\right)^2 = \frac{4K_h g \Delta \rho F t}{\phi \bar{\mu} h}$$  \hspace{1cm} 4-19

$F$ is a complex function of the viscosities of the two different fluids involved. However, as mentioned earlier in this work we assume that both fluids have the same viscosity and therefore $F$ is equal to one. Eq. 4-18 and 4-19 are combined to give a solution of the length of the interface ($2x$) at different times (early, intermediate and late):

$$\left(\frac{2x}{h}\right)^2 = \frac{16}{3} F^2 \frac{K_h}{K_v} \frac{(t/t_0)^2}{1 + t/t_0}$$  \hspace{1cm} 4-20

where $t_0$ is the characteristic time which determines the rate at which the mixing takes place. It is defined by

$$t_0 = \frac{4 \phi h \bar{\mu} F}{3 K_v g \Delta \rho}$$  \hspace{1cm} 4-21

### 4.3.2 Numerical Simulation in a Rectangular Geometry

To compare the analytical solutions presented above to the results from our numerical model generated using the reservoir simulator package (CMG STARS), a simple rectangular cross section reservoir model is used. The reservoir has been filled from the left and this is represented by two different fluids of different density filling different compartments of the reservoir, with a vertical interface between them. For simplicity, the oils are assumed to be incompressible and there is no mobile water within the reservoir.
4.3.2.1 Horizontal Model

To compare mixing times from our simulations with the analytical solutions from Eq. 4-20, we initialized a rectangular domain with a binary mixture of nC₆/ nC₁₂ separated by a vertical interface. The left half of the domain was saturated with the lighter component while the right half was filled with the heavier component. To induce the gravitational overturning process, we imposed a density difference between the regions of 10 kg m⁻³ (the density of nC₁₂ was set to 800 kg m⁻³ while that of nC₆ was set to 790 kg m⁻³). We also altered the viscosity of the components, making them equal so that the interface remains as a plane surface (therefore, \( F = 1.0 \) in Eq. 4-20). To reduce the effect of numerical dispersion in our simulation we used very fine grids. The gridding in this example (and the rest of the chapter) is set to 200 × 1 × 200. This gridding was chosen after the grid refinement exercise which we shall show later on in this section (see Fig. 4-4). Table 4.1 shows the input parameters used for this exercise. Here we used parameters similar to those in the work by England et al. (1995).

Table 4-1: Reservoir and fluid properties for the gravitational overturning simulations.

<table>
<thead>
<tr>
<th>Reservoir Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
<td>200 × 1 × 200</td>
</tr>
<tr>
<td>Dimensions</td>
<td>2000 m × 1 m × 100 m</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.2</td>
</tr>
<tr>
<td>Vertical Permeability</td>
<td>100 mD</td>
</tr>
<tr>
<td>Horizontal Permeability</td>
<td>100 mD</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluid Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Viscosity</td>
<td>( 1 \times 10^{-3} ) pa.s</td>
</tr>
<tr>
<td>Density difference</td>
<td>10 kg m⁻³</td>
</tr>
</tbody>
</table>

Figure 4-3 shows the density distribution at different times for the density driven convection process. It can be observed in the figure, there is still some spreading at the interface which
should be sharp. We have tried to mitigate the numerical dispersion by using fine grids but this cannot be completely removed. Improved sharpness of the interface can be achieved by using finer grids but this would require more computational effort and increase simulation time. However, this would not improve the position of the interface (see Fig. 4-4). To compute the position of the interface for the less fine grids, we use the average density of the two fluids. Figure 4-4 compares the values of the parameter $2x/h$ from the reservoir simulator to the analytical solution. It can be observed that there is a slight discrepancy between the two results (using the fine grid of $200 \times 1 \times 200$). The reservoir simulator always under predicts the gravitational overturning mixing time.

As mentioned earlier, it is assumed in the derivation of the analytical solution of Gardener et al., (1962) that the interface is a plane surface. However, the result from simulator shows that the interface is slightly curved, especially at the vertical boundaries. We notice that if we consider the $2x/h$ as the slope of the interface at the centre (where the interface is linear, see Fig. 4-5), the agreement between the simulator and the analytical solution improves significantly, Figure 4-6.
Figure 4-3: Density distribution and motion of the interface from the CMG STARS® simulations at different times.

Figure 4-4: Comparison of the gradient of the interface from the CMG STARS® simulations with the analytical solution of Gardner et al., (1962).
Figure 4-5: Calculating the slope of the interface at the centre of the domain in order to treat the interface as a plane surface.

Figure 4-6: Comparison of the results from our numerical simulations when the interface is treated as tangent lines with the analytical solution of Gardner et al., (1962).

To determine the time to achieve steady state for the gravitational segregation process described above, we use the density gradient metrics defined by Eqs. 4-16 and 4-17. Figure 4-7 shows how the average vertical and lateral density gradients change with time. This plot can be used solely to describe the gravitational overturning process. We observe that a vertical density gradient increases then reaches its plateau first. Recall that this parameter was computed using average values from the top and bottom layer of the reservoir, therefore this signifies the point where the light component fully occupies the top layer of the domain, and
the heavier fluid the bottom half. The lateral density gradient on the other hand remains constant during the initial stage of gravitational overturning and only begins to decrease when the interface has reached the vertical boundaries. The lateral gradient then reduces until steady state is attained. England et al., (1995) proposed that the steady state for the density driven overturning process occurs when the mixing parameter \((2x/h)\) is equal to 100 (this is equivalent to a 80% reduction in the lateral density gradient). The steady state of this system occurs at approximately 34,000 yrs (this corresponds to a density difference of \(8\times10^{-4}\) kgm\(^{-3}\)).

![Figure 4-7: Gravitational overturning process described using the change in lateral and vertical density gradient over time (the red curve represent the vertical gradient, while the blue is the horizontal).](image)

### 4.3.2.2 Inclined Model

The other extreme case is a vertical model (where the vertical dimension is larger than the horizontal dimension) is more complicated, as this introduces the problem of viscous fingering. If the model was initialized with the heavy fluid on top of the light one, the subsequent motion is greatly influenced by whatever small perturbations may exist in the model. Gardner et al., (1962) derived a solution for a vertical system with a bias by setting the interface at a plane inclined at about 45° to the x-axis. This solution is found to fit their experimental results, however this solution were empirical as there were no theoretical justification of the results. As a result of this and the fact that most typical reservoirs have a width larger than the thickness, we do not carry out any investigation of gravitational overturning in a vertical model.
Gardner et al., (1962) also investigated a horizontal model where the $x$-axis is inclined at an angle $\alpha$ with respect the horizontal, in which convection occurs as a result of density gradients. By resolving the horizontal and vertical component of the acceleration of gravity, the motion of the fluid can be considered as a combination of flow in the vertical model due to a density difference $\Delta \rho \sin \alpha$ and a flow in the horizontal model due to the density difference $\Delta \rho \cos \alpha$. Combining this two motions, they obtain a formula for the length:

$$\frac{x}{h \cot \alpha} - \ln \left(1 + \frac{x}{h \cot \alpha}\right) = \frac{k_h g \Delta \rho t \sin \alpha}{2 \varrho \mu h \cot \alpha}$$ 4-22

This equation reduces to Eq. 4-20 when $\alpha$ is small. To analyze the validity of the mixing time of our inclined model, we simulate experiments carried out by Gardner et al., (1962) for a rectangular cross section with two different tilting angles ($5^\circ$ and $45^\circ$) and then compare the results to that obtained in their work and to the analytic solution Eq. 4-22. The relevant data for this exercise are shown in Table 4.2. We chose to simulate a similar system to that studied by Gardner et al., (1962), so that we could compare the results obtained from our simulations to that from both experimental work and the analytical solution.

Table 4-2: Parameters for gravitational overturning in inclined models.

<table>
<thead>
<tr>
<th>Reservoir Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
<td>$400 \times 1\times 50$</td>
</tr>
<tr>
<td>Dimensions</td>
<td>$366 \text{ cm} \times 0.412 \text{ cm} \times 10 \text{ cm}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.36</td>
</tr>
<tr>
<td>Horizontal Permeability</td>
<td>44.2 D</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluid Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Viscosity ratio ($\mu_2/\mu_1$)</td>
<td>$\sim 1.01$</td>
</tr>
<tr>
<td>Density difference</td>
<td>562 and 571 kg m$^{-3}$ for ($5^\circ$ and $45^\circ$)</td>
</tr>
</tbody>
</table>
Figure 4-8 shows the results for this exercise; we observe that there is a good agreement between our simulation results and the experiments carried out by Gardner et al., (1962) with an average absolute deviation (AAD) of 0.4%. The difference in the start time between the systems with the two different angle of inclination is most likely due to the initial slope of the interface. This would lead to different lateral density gradients for the two cases as we observe in section 4.4.5. There is also a satisfactory agreement with the analytical solution. The numerical simulations seems to match the analytical solution (the solid line) at late times, however there are discrepancies at early times. This is not surprising as the analytical solution has been derived for intermediate to late times. We also observe that the discrepancies become larger when the angle of inclination increases.

![Graph showing motion of interface due to gravitational overturning for inclined models.](image)

Figure 4-8: Motion of interface due to gravitational overturning for inclined models.

### 4.3.3 Validation of Molecular Diffusion Mixing Time

Having confirmed the timescales for gravitational overturning predicted by the analytical solution and by the reservoir simulator, it is important to investigate how the other flux we are interested in, molecular diffusion, might alter the timescales of density overturning.
Before we investigate this, we have to make sure that the reservoir simulator accurately models this flux.

Crank(1975) derived an analytical solution for the transient compositional profiles for an equi-molar binary mixture under the influence of molecular diffusion in a closed system. This solution only holds for a binary mixture that only differs in the molecular weight. The domain is initialized with different composition of the species in the different compartments of the domain as shown in Fig. 4-9. This initial condition can be expressed as:

\[ x_1(l, 0) = \begin{cases} 
  x_1 & \text{for } 0 < l < b \\
  x_2 & \text{for } b < l < L 
\end{cases} \tag{4-23} \]

The transient and steady state composition profiles can be computed analytically using Eq. 4-24:

\[
x_i = \frac{x_1 - x_2}{2} \sum_{n=-\infty}^{\infty} \left[ \text{erf} \left( \frac{b + 2nL - l}{\sqrt{4Dt}} \right) + \text{erf} \left( \frac{b - 2nL + l}{\sqrt{4Dt}} \right) \right] + x_2 \tag{4-24}
\]

where \( L, D \) and \( t \) are the characteristic length of diffusion, molecular diffusion coefficient and the time.
To validate the molecular diffusion mixing feature of CMG STARS® using the Eq. 4-24, we considered a binary system with the same dimensions as that used in section 4.3.2. However the vertical and horizontal permeability values were reduced significantly in order to simulate molecular diffusion alone (see Table 4.3). The densities of the two components of the mixture are set to be equal, in order to simulate an equi-molar volume mixture. The domain is split into two equal compartments as shown in Figure 4-9. We initialize the reservoir with \( nC_{12} \) and \( nC_{12}^* \) (same molar volume as \( nC_{12} \) but has an increased molecular weight) with a 90:10 composition ratio in the right hand side and 20:80 ratio in the left hand side. The two components only differ in molecular weights. A typical value for molecular diffusion coefficient for liquid mixtures of \( 1.7 \times 10^{-8} \text{ m}^2\text{s}^{-1} \) was used in this exercise. In CMG STARS® does not compute the molecular diffusion coefficient; a constant value is inputted for this parameter. In Appendix A6, we show that this is a valid approach as the variation in molecular diffusion coefficient produces a negligible change in composition.

Table 4-3: Reservoir and fluid properties for the molecular diffusion mixing time validation exercise.

<table>
<thead>
<tr>
<th>Reservoir Properties</th>
<th>200 × 1 × 200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
<td></td>
</tr>
<tr>
<td>Dimensions</td>
<td>2000 m × 1 m × 100 m</td>
</tr>
<tr>
<td>Porosity</td>
<td>1</td>
</tr>
<tr>
<td>( K_v = K_h )</td>
<td>1 × 10^{-10} mD</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Fluid Properties</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid components</td>
<td>( nC_{12} ) and ( nC_{12}^* )</td>
</tr>
<tr>
<td>Molecular weights</td>
<td>170.34 and 282.56 (g/mole)</td>
</tr>
<tr>
<td>Datum fluid composition</td>
<td>0.2 and 0.8 (left compartment)</td>
</tr>
<tr>
<td></td>
<td>0.9 and 0.1 (right compartment)</td>
</tr>
</tbody>
</table>

Figure 4-10 shows the composition of \( nC_{12} \) after the 100,000 years. It can be observed that the fluid interface spreads as the molecules diffuse; this will eventually result in a uniform mixture at steady state. Figure 4-11 compares the results for the change in \( nC_{12} \) composition.
profile with time obtained from CMG STARS® and the analytical solution (Eq. 4-24). It can be observed that timescales for the mixture to reach equilibrium under the influence of molecular diffusion is a lot longer than that of the gravitational overturning process. The results obtained from the reservoir simulation model are in good agreement with that predicted from the analytical solution (maximum deviation of 0.034 was observed for all timescales; when comparing difference between the mole fractions from the simulation to the analytical solution for each node). Note that in the analytical solution, Eq. 4-24, it was sufficient to have only 11 terms in the summation for this exercise.

![Figure 4-10: Mole fraction distribution of nC₁₂ after 100,000 years of diffusion mixing.](image)

![Figure 4-11: Comparison of the results of the numerical solution from CMG STARS® for the nC₁₂ composition with the analytical solution for diffusion mixing at different times (M Yrs = million of years).](image)
Figure 4-12, shows the plot of how the species separation metric (Eq. 4-15) changes with time. We can observe that the plot decreases from the initial separation of 0.8 until it reaches steady state at about 5 million years. For this exercise steady state was defined as when the composition difference is 0.01 times its original value. Compared to that of gravitational overturning, the timescales of molecular diffusion is as expected quite large (several orders of magnitude larger than that of the convection process which was approximately 30,000 years for a similar reservoir configuration).

![Diagram showing species separation metric](image)

Figure 4-12: Species composition metric for the numerical simulation validation exercise.

### 4.4 Results for 2D Rectangular Model

Having validated density driven convection and molecular diffusion mixing times in the CMG STARS® model, we now conduct a sensitivity analysis to see what impact several different parameters which are usually present in hydrocarbon reservoirs will have on the separation-mixing process. In the validation exercise we assumed that the reservoir was homogenous (no barriers to flow) with no thermal gradient. This is not the case in real-life. We therefore select a few conditions that are usually present in most reservoirs and see how they affect the steady state composition and the timescales. In this section, we shall quantify the motion and behaviour of the fluids using the metrics described in section 4.2.1.
4.4.1 Gravity Segregation

For this exercise a 2D horizontal rectangular porous medium with a width of 2000 m and height of 100 m is saturated with a binary mixture of $nC_{12}$ and $nC_{24}$. We initialize the system with the two species completely separated from each other; with the denser fluid on the right-hand part of the domain. As we are simulating a porous mixture, we set the value of the term $1/F\Phi$ (in Eq. 2-6) to be equal to 0.34 (based on values of tortuosity factor and cementation exponent for average sandstone reservoirs (Carrothers, 1968)) and multiply the molecular diffusion coefficient by this value, in cases where the molecular diffusion is being implemented. The purpose of these simulations is to investigate the impact typical reservoir characteristics would have on the compositional variation of a mixture under the influence of diffusion and convection. Table 4.4, summarizes the parameters used for all the simulations.

We initially modelled fluid flow due solely to density driven convection. We assume that the reservoir has constant temperature of 373 K, and the pressure field is calculated assuming vertical equilibrium. As we illustrated earlier this would lead to the gradual tilting of the interfaces towards its equilibrium (horizontal position) as time progresses, see Fig. 4-13. Figure 4-14 (a) and (b) show the density gradients and the composition separation metrics. The later metric remains constant throughout the duration of the simulation because there is no compositional mixing by molecular diffusion. The density gradients describe the convection process as explained in Section 4.3.2 and it can be observed that this system reaches steady state at about 25,000 yrs (the lateral density gradient levels to a plateau).
Table 4-4: Reservoir and fluid properties for the gravitational overturning and molecular diffusion analysis.

<table>
<thead>
<tr>
<th><strong>Reservoir Properties</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
<td>$200 \times 1 \times 200$</td>
</tr>
<tr>
<td>Dimensions</td>
<td>$2000 \text{ m} \times 1 \text{ m} \times 100 \text{ m}$</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.25</td>
</tr>
<tr>
<td>Permeability</td>
<td>100 mD</td>
</tr>
<tr>
<td>Datum Temperature</td>
<td>373 K</td>
</tr>
<tr>
<td>Datum Pressure</td>
<td>1500 kPa</td>
</tr>
<tr>
<td>Temperature gradients</td>
<td>0.03 K/m and 0.001 K/m (Isothermal)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Fluid Properties</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluid Viscosity</td>
<td>$1 \times 10^{-3} \text{ pa.s}$</td>
</tr>
<tr>
<td>Fluid Components</td>
<td>$nC_{12}$ and $nC_{24}$</td>
</tr>
</tbody>
</table>
Figure 4-13: Plot of density distribution at different times for a system under density driven convection.

Figure 4-14: Metrics for the gravitational overturning process.
4.4.2 Impact of Molecular Diffusion (Base Case)

The previous exercise on the effect of molecular diffusion alone shows that this flux will lead to the spreading of the interface until the mixture is completely homogenous. In this section, we investigate the effect of molecular diffusion in a system where natural convection is also acting. We use the same mixture and reservoir as the previous case for this exercise. A molecular diffusion coefficient of $3.3 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ calculated using the correlation proposed by Leahy-Dios and Firoozabdi (2007) for the binary mixture was used for this simulation (see Appendix A4). Figure 4-15 shows the fluid distribution changes with time when the effects of molecular diffusion are included in the simulation. A comparison with the distribution for the same time (Figure 4-13) without diffusion shows that the originally sharp interface has been spread out significantly and the overall compositional difference in the domain has decreased considerably. This would have an impact on the rates of mixing by convection and diffusion as the driving forces for these processes are composition gradients.

![Figure 4-15: Density distribution in the 2D domain for a system under the influence of natural convection and molecular diffusion.](image-url)
Figure 4-16(a) shows how the vertical density gradient changes with time; we observe that this plot is very different from that obtained from the previous case. The vertical gradient initially increases and then reaches a maximum at 0.10 (approx. 18,000 years) before decreasing to its steady state value. The initial increase can be attributed to convection dominated flow in the system, whilst the decrease in this parameter suggests that molecular diffusion is the main flux governing the mixing of the mixture. This hypothesis is reinforced by the observation made in Fig. 4-16(b), where it can be seen that the separation metric starts to decline after 18,000 years. The drop in this metric is indicative of mixing by molecular diffusion. It should be noted that comparing the maximum point of the vertical density gradient plot to that of the initial case with only density driven convection (see Fig. 4-17(a)), one observes that the maximum value of the former is less because diffusion takes place before the two fluids have enough time to completely segregate. The steady state time of the system has been increased from 45,000 years in the convection only system to about 3 million years (Myrs). This can be observed from Fig. 4-16(b) where the $nC_{12}$ separation levels off to its minimum value.

The rate of gravitational overturning has been slowed down in the system because of the molecular diffusion mixing of the two mixtures; this can be observed by the decline in the rate of change of the density gradients. Fig 4-17(b) compares the horizontal density gradient of this system to that of the ‘convection only’ case. At early times, we observe that the horizontal density gradient starts decreasing from its initial value (0.071) after 9500 years. This is approximately thousand years earlier compared to the case under the influence of convection and diffusion. The rate at which density gradient decreases is slower than in the case with diffusion and convection and it takes double the amount of time for this parameter is decrease to 0.003.

It is very important to note that if we use order of magnitude estimates listed in Table 2-1 to calculate the timescales for diffusion alone in this system, we find that the fluid mixing occurs at a faster rate, 3 Myrs compared to 30 Myrs. This demonstrates the importance of studying the combined convection and diffusion effects in estimating the steady state time. The system under the influence of molecular diffusion and density driven convection will be treated as our base case from this point on.
Figure 4.16: The change in density gradients and $nC_{12}$ separation with time in a system under the influence of density driven convection and molecular diffusion. This figure shows that the system reaches steady state at approximately 3 Myrs.

The reader is reminded that the fluid mixture density is calculated assuming ideal mixing; therefore the density is inversely proportional to the species composition. Thus, the lateral density gradient and the species (composition) separation metric will have the same signature.
as the fluid mixes. In the subsequent exercise, we shall use one of the two metrics to determine the equilibrium time.

![Graph showing density gradient over time for two scenarios: Convection Only and Convection and Diffusion.](image)

(a) Vertical Density Gradient  
(b) Lateral Density Gradient

Figure 4-17: Comparison of the density gradients at early times for study the impact of molecular diffusion on the fluid mixing process.

### 4.4.2.1 Impact of Molecular Diffusion Coefficients

It is important to point out that if the molecular diffusion coefficient of the mixture was reduced, this would lead to a more density driven dominated flow regime as the rate of molecular diffusion mixing decreases. Figure 4-18 illustrates this, as it shows the fluid distribution at 25,000 years for a system where the diffusion coefficient has been reduced by an order of magnitude ($3.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}$). We observe that there is less smearing of the interface and the fluid movement due to convection current is more pronounced.

The approximate expression for the timescales for a system under the influence of molecular diffusion to reach steady state suggests that the time to attain steady state is inversely proportional to the diffusion coefficient ($t = L^2/D$), thus reducing the diffusion coefficient should lead to a later equilibrium time. However in a system under the combined influence of convection and diffusion, having a smaller diffusion coefficient can lead to a faster steady state time. This is the case in our system. Figure 4-19, compares the $nC_{12}$ mole fraction separation of the two cases with different molecular diffusion coefficients. The initial stage of
the mixing process for the case with a smaller diffusion coefficient is dominated by convection; this is evident in the slower rate in the decline in the species separation. This would lead to the diffusion mixing occurring over the shorter vertical distance (100 m) as the overturning process has already occurred. Thus, the system with the smaller molecular diffusion coefficient reaches steady state at about 1 Myrs compared to approx. 3 Myrs for a system with larger diffusion coefficient. Increasing the molecular diffusion coefficient would have an opposite effect (increasing mixing timescale), as this would make the system diffusion dominated. This in-turn would lead to an increase in the time to attain steady state (as the grading occurs over the longer lateral distance, 2000 m). This exercise points out the importance of modelling both diffusion and convection with an accurate knowledge of the diffusion coefficient and fluid properties.

\[
\text{Time} = 25,000 \text{ yrs}
\]

Figure 4-18: Fluid distribution in the 2D domain after 25,000 years in the system (with reduced molecular diffusion coefficient of \(3.3 \times 10^{-10} \text{ m}^2\text{s}^{-1}\)).

Figure 4-19: Impact of reducing the molecular diffusion coefficient illustrated using the \(nC_{12}\) separation metric.
4.4.3 Impact of Different Initial Compositions

4.4.3.1 Effect of Initial Composition Difference

Hydrocarbon fluids emitted from source rocks prior to mixing usually contain a mixture of two or more components, as opposed to having the components of the mixture completely initially segregated (as implemented in the previous cases). To study the impact this different initial composition would have on the mixing time, we simulate a case with the same configuration as the base case; however we initialize the right and left hand side of the domain with a 25:75 and 75:25 composition ratio of $nC_{12}$ and $nC_{24}$ respectively. This would lead to a smaller initial composition and density difference in the system.

![Figure 4-20: Initial $nC_{12}$ composition distribution in the 2D domain.](image)

To illustrate the impact this has on the timescales to reach equilibrium we plot the $nC_{12}$ separation metrics for both cases against time (Fig. 4-21). We observe that there is a negligible change in the steady state time when the initial composition difference has been halved from 100% to 50% (the two curves are super-imposed after approx. 1.5 Myrs). This is due to the reduction in the initial mixing rate (via convection and diffusion) when the composition difference is smaller (the mixing rates for these fluxes are directly proportional to the initial composition difference).
4.4.3.2 Impact of Graduated Oil Properties

A real reservoir is unlikely to start off with two fluids of different properties separated by a sharp interface. It is argued in literature that there will be some mixing while the reservoir is being charged. This means that a more realistic depiction of the initial state of the reservoir is one where the fluid density varies linearly with distance in the direction of filling (Fig. 4-22).

Figure 4-22: Initial $nC_{12}$ composition distribution in the 2D domain (initial graduated mole fraction).

Figure 4-23 shows the comparison of the horizontal density gradient for the different initial conditions at the early stages of the simulation. Note that the initial lateral density gradient has been reduced from 0.007 to 0.0057. However, the base case with a higher density
gradient mixes quicker than the case with graduated initial composition. Figure 4-23 highlights this decline in the initial mixing rate. However the change in the time to reach steady state in the two cases is negligible; it is shown that after about 0.8 million years the two curves overlap.

![Figure 4-23: Comparison of the lateral density gradient of the base case and the case with initially graduated composition distribution.](image)

**4.4.4 Impact of Heterogeneity**

It is well established that reservoir permeability plays a key role on the magnitude and direction of fluid flow in the petroleum reservoir given a production timescale. Although, Darcy velocity is smaller in reservoirs prior to production the effect of heterogeneity and anisotropy which in turn affects reservoir permeability is still very important.

**4.4.4.1 Impact of Anisotropy and Permeability Layering**

In previous cases, we have assumed the domain was homogenous. Most reservoir rocks are layered, with layers having a different permeability. High permeable reservoir layers are usually inter-bedded with poorer reservoir rocks. We have also previously assumed the permeability to be isotropic; this is not usually the case in real hydrocarbon systems. We introduced 5 horizontal layers with different permeability in the domain to study the effect of permeability layering. We also included permeability anisotropy of $K_v/K_h = 0.1$, where $K_v$ and $K_h$ are the vertical and horizontal permeability, respectively. Figure 4-24 shows the distribution of the horizontal permeability in the reservoir. The horizontal permeabilities of
the layers are 100, 10, 50, 10 and 100 mD from top to bottom. This distribution is analogous to good reservoir rock inter-bedded by poorer less permeable rocks. The thickness of each layer is the same.

Figure 4-24: Horizontal Permeability ($k_h$) variation in the 2D domain.

Figure 4-25, shows the effect of the permeability heterogeneity and anisotropy on the oil distribution after 25,000 years. We notice that the rate of gravity overturning has been significantly reduced as the interface has not reached the vertical boundaries of the domain yet (compared to the base case, Fig 4-15), however that the smearing of the interface due to diffusion has become more pronounced.

Time = 25, 000 yrs

Figure 4-25: Fluid distribution in the layered 2D domain after 25,000 years.
A comparison of the change of lateral density gradient with time (at early times) for the layered and homogenous system is shown in Figure 4-26(a). This confirms that the rate of gravitational overturning has slowed down as it takes longer for this metric to reduce from its original value (50,000 years compared to 7,500 years in the base case). Figure 4-26(b) shows the comparison of this metric for both systems at late times (until equilibrium is attained). It is observed that the heterogeneous reservoir takes an extra 7 million years to reach steady state. We conclude that reduction in reservoir quality leads to a longer equilibrium time, as the gravitational overturning process is significantly reduced, thus leading to mixing occurring mainly by diffusion over a longer lateral distance.

Figure 4-26: Lateral density gradient metric ($D_x$) for the homogenous and layered 2D domain at early and late times.

**4.4.4.2 Impact of Shales**

The effect of the inclusion of a stochastic shale distribution with reduced effective vertical permeability (three orders of magnitude less than the base case) has also been studied. The shale distribution was modelled in the simulation program by transmissibility barriers. The shale distribution as shown in Figure 4-27, was constrained so that at least one grid block separated each shale. This configuration is similar to that used by England et al., (1995). The fluid and rock properties were otherwise unchanged from the base case.
Figure 4-28 shows the oil distribution in the shaley reservoir after 25,000 years. There was little difference when compared with the base case. The shape of the interface has however been slightly distorted.

Figure 4-27: Shale distribution in the 2D domain.

Figure 4-29 which shows the change of horizontal density gradient with time provides a better way of comparing the rate of mixing to the homogenous domain. From this plot we can clearly see that introducing the stochastic shales into the domain decreases the fluid mixing time. It is observed that the initial value of this metric decreases at a later time and the system reaches equilibrium 3 million years after the homogenous system. The reader is reminded that the heterogeneity are modelled by only a reduction in permeability, if the reduction in porosity is also investigated the timescales will be further increased as the rate of molecular diffusion will be reduced.

Time = 25,000 years

Figure 4-28: Oil mass density distribution in the shaley reservoir after 25,000 years.
4.4.5 Impact of Inclination

Hydrocarbon fluids are usually trapped in tilted reservoirs or *anticlinal* traps. We investigated the impact of this different reservoir configuration by simulating two cases with similar rock and fluid properties as the base case, inclined at angles 5° and 15°. In a tilted reservoir with the light fluid on top of the heavy (see Fig 4-30 (a)), mixing initially occurs due to natural convection. This leads to the interface tilting from a vertical position till its flat (which happens very quickly) and then subsequent mixing by convection and diffusion (see Fig 4-30 (b)). Figure 4-31, shows the change of the horizontal density gradient with time for the horizontal and two inclined models.
Figure 4-30: Density distribution in the inclined domain at different times.

Figure 4-31: The change of lateral density gradients with time for the horizontal and inclined configurations at early (<1myrs) and late times.
The reader should notice that in this figure, the initial value of this metric increases as the system becomes more inclined. This is due to the increase in elevation as the system becomes tilted; and as the domain is initialized with the vertical depth averaging method, the density difference will also increase. From this plot, we observe that reservoir tilting affects the fluid mixing timescales. The rate of mixing is a lot slower as the 2D domain becomes more inclined. This is due increased elevation due to reservoir tilting, thus the fluid mixing occurs over a longer *vertical* path. From figure 4-31, we observe that the different cases level off at different steady state values; this is due to the different elevation of the systems as explained earlier. To provide a better comparison of the equilibrium timescales, we plot the species separation metric of $nC_{12}$ over time. This plot also shows that the equilibrium mixing time has been increased when the system is inclined. It takes an extra 2 million years and 7 million years for the systems inclined at 5° and 15° to reach steady state respectively.

![Graphs showing species separation metric for different inclinations](image-url)

(a) Early times | (b) Late times

*Figure 4-32: $nC_{12}$ separation metric for the horizontal and inclined models.*
4.4.6 Impact of Thermal Gradients

In addition to the gravitational overturning process caused by the concentration gradient in the system, convection can also occur due to density gradients induced by temperature gradients in the subsurface. This process is referred to as thermal convection. The onset of this process is governed by the critical Rayleigh number. As explained in section 2.3.1 when this dimensionless number exceeds approximately 39 ($4\pi^2$) for a fluid, thermal convection sets in.

When carrying out conventional reservoir simulation, a uniform temperature profile is usually imposed. This however not the case as vertical geothermal gradients are always present in hydrocarbon reservoirs. Some reservoirs have also been known to have a lateral temperature profile. To investigate the effect of thermal gradients we simulate a horizontal 2D domain with the same rock and fluid properties as the previous cases, with a vertical and horizontal temperature gradient of 0.03 K/m and 0.001 K/m, respectively (Figure 4-33). These values are typical to that in many hydrocarbon fields (Nasrabadi and Firoozabadi, 2005). Over the range of temperature and pressure for this reservoir, the fluid remains a single phase mixture. This configuration would lead to stable fluid system as the vertical and horizontal Rayleigh number of 0.38 and 0.24 (less than $4\pi^2$).

![Figure 4-33: Temperature profile in the 2D domain (units: °C).](image)

Figure 4-34 shows the mass density distribution in the domain after 25,000 years. We observe that this profile is quite similar to that of the base case (with homogenous temperature field). We see the signature of convection and the spreading of the interface due to diffusion; however the rate of mixing has been reduced. This is illustrated better by comparing the $nC_{12}$ separation metric for the two cases (Fig. 4-35). We opt to use the separation metric as this
will provide a better comparison with the base case, as opposed to the density gradient which will be altered by the temperature gradient present in the system.

We observe that in this case the temperature gradient slows down to the mixing process by convection and diffusion and the equilibrium time has been increased by about 13 million years.

\[
T = 25,000 \text{ years}
\]

Figure 4-34: Oil distribution after 25,000 years for the 2D system with lateral and vertical geothermal gradients.

Figure 4-35: Comparison of the nC_{12} separation metrics for the system with uniform and regular thermal gradients.
We conclude that in this system that the temperature gradients which are typical of hydrocarbon reservoirs will have significant effect on the equilibrium mixing time. Some reservoirs could be more laterally extensive (width greater than 2000 m) or have unusually high geothermal gradients. In these systems the rate of mixing by convection will be affected more as the Rayleigh number will exceed its critical value. This will lead to instabilities in form of oscillations in the reservoir. We thus simulated a case with un-realistic temperature gradients to illustrate this point. Figure 4-36 shows a system with a vertical and horizontal temperature gradient of 0.09 K/m and 0.03 K/m, respectively.

Figure 4-36: Unusual geothermal gradient in the 2D domain.

Figure 4-37 shows the oil distribution in this system after 10,000 years. We notice a drastic difference compared to the system with uniform temperature field. The impact of convection due to thermal gradient is evident especially around the lateral boundaries. Comparing the metrics of this case to the base case, we notice that the increased temperature gradient decreases the initial rate of fluid mixing in the system. However the mixing rate increases at later stages given a more homogenous steady state mixture compared to the other two cases after 5 Myrs. The equilibrium mixing time for the system with abnormal thermal gradients has only increased by a million years.
Figure 4-37: Oil mass density after 10,000 years for the case with unusual temperature profiles.

Figure 4-38: Comparison of the $nC_{12}$ separation metrics for the system with uniform and “un-realistic” thermal gradients.

4.5 Chapter Summary

We have studied the dynamics of the fluid mixing process by natural convection and molecular diffusion in a two-dimensional porous medium. The modelling of these processes by the reservoir simulation package used for this exercise, CMG STARS®, was initially
verified using analytical solutions for gravitational overturning and molecular diffusion derived by Gardner et al., (1962) and Crank (1975), respectively. We then performed a sensitivity analysis on different conditions which are present in typical hydrocarbon reservoirs, to see how they affect the equilibrium mixing timescales. We found that reservoir tilting and heterogeneity had an adverse effect on the fluid mixing process. While changing the initial composition had a negligible effect on the rate of mixing in the studied system. The inclusion of temperature gradients and solving the energy equation may enhance or hinder the mixing process. This exercise pointed out the importance of studying the impact of natural convection along side with the diffusion process as we observed that the convection process significantly reduced the time to reach steady state, compared to the cases were fluid mixing was due to molecular diffusion alone.
Chapter 5

Field Study: Compositional Variation in the LaBarge Field (Madison Reservoir)

Gas containing a high amount of carbon dioxide (approximately 66%) was discovered in the Madison formation in the Greater Green River Basin in Wyoming, U.S.A when the Paleozoic rocks were first explored by Mobil Oil Company in 1961. The gas composition in this reservoir also varies significantly within the reservoir. The carbon dioxide (CO\(_2\)) composition in this field varies from 5% at the crest of the structure to 90% at the gas-water contact (GWC). Methane (CH\(_4\)) the second most significant component in the Madison varies from 23% at the crest to 5% at the GWC. The unusual composition and gradient of this reservoir has been a subject of investigation for different authors (Huang et al., 2007; Stilwell, 1989 and Becker and Lynds; 2012) in the context of CO\(_2\) sequestration and the management of the acid gas injection plant in the LaBarge Field. Only Huang et al., (2007) have investigated the fluxes that lead to the current gas composition gradient in the Madison formation.

If the observed compositional distribution in this reservoir can be reproduced by the previously defined fluid mixing techniques (Chapter 3 and 4), one can use this as a basis to build reservoir models to determine whether this structure and neighbouring formations can be developed economically. The Madison formation is a relatively continuous reservoir. Therefore this reservoir will serve as a useful test to explore whether the fluid mixing model and analytical solution can be used to explain fluid distribution in reservoirs. This will help
build confidence that these same methods can be used to indicate compartmentalization in other fields. In this chapter, we shall thus use both the 1D and 2D (CMG STARS®) models discussed in the previous chapters to investigate reason behind the current composition profile present in this formation and the timescales required to reproduce the current profile.

5.1 Field Description

The LaBarge Field is located at the northwestern crest of the Moxa Arch anticline as shown in Figure 5-1 (Benge and Dew; 2005 and Huang et al., 2007). The Madison Limestone formation which is the primary pay interval of the LaBarge Field is the main interest of this study. The Moxa Arch is a north south trending anticline located in the western part of the Greater Green River Basin, southwest Wyoming (Figure 5-1). This major structure is approximately 130 miles long (Becker and Lynds, 2012), and contains nine gas and oil formations that have large amounts of CO₂ in the Paleozoic section. In 1961, several exploration wells by Mobil Oil Company that penetrated the Madison formation discovered sour gas with large percentage of CO₂ (65%). Additional periodic testing has shown that seven of the nine Paleozoic formations (all formations apart from the Weber Sandstone and Gallatin Limestone) contain CO₂ rich gas at multiple locations. The stratigraphic correlation chart of the Paleozoic section in the western Green River Basin, showing all the nine formations is shown in Appendix A7. The production of the sour gas in this region however did not commence till 1986, when the LaBarge gas plant was commissioned by Exxon Mobil.

Several authors (De Bruin; 2001, Stilwell; 1989 and Becker and Lynds; 2012) have come up with different theories to explain the unusually high concentration of CO₂ in the southwest Wyoming region. The shales of the Phosphoria formation are believed to be the source rock for most of the Paleozoic formations (Stilwell; 1989) in the anticline. The generation of hydrocarbon (dead oil) was believed to have started about 150 Ma (Jurassic era) in the Idaho area and then migrated to the east towards the Green River Basin (Stilwell; 1989). Subsequent thermal degradation of the liquid hydrocarbons has led to large gas accumulations that contain CO₂ and H₂S. It is proposed that a further increase in the percentage of CO₂ in the formations may be as a result of quaternary-tertiary volcanic activity that occurred in the Rock Springs Uplift (Becker and Lynds; 2012). After CO₂ generation, the gas migrated to the Moxa Arch.
It is also believed that the sour gas is in part also a result of inorganic thermo-chemical sulphate reduction (ITSR) that occurred in the Paelozoic formations. This is a reaction between the anhydrite and methane that produces CO\textsubscript{2} and H\textsubscript{2}S (Hill, 1990). This theory is backed by the fact that most of the formations in the Arch contain anhydrite beds. From burial history curves for the central Moxa Arch (Roberts et al., 2005), Becker and Lynds (2012) stated that appropriate depths or temperatures were likely to be reached between the Campanian (80 Myrs ago) and the Eocene (50 Myrs ago). This uncertainty in the timescales is due to the complicated burial history in the Green River Basin region.

![Figure 5-1](image_url)

**Figure 5-1:** Map showing the Location of the LaBarge Field area and the surrounding structural settings in the Greater Green River Basin in south western Wyoming. MA indicates the Moxa Arch Anticline (Huang et al., 2007).

The Madison Limestone reservoir in the LaBarge Field, Wyoming United States is a low angle multi-zone carbonate reservoir deposited in the Mississippian age (approximately 330 million years ago). The productive area of the Madison spans an area of about 34 km by 105 km, as shown in figure 5-3(a). There is enough information to describe the lithology of and
reservoir character of the Madison as this reservoir has been developed since 1986 and is the most studied formation in the Paleozoic section.

The productive area of the Madison consists of alternating dolomite and anhydrite sequences inter-bedded with limestone. The limestone generally exhibit low porosity (< 6%), while the dolomite layers have a higher porosity (6% ≥ φ ≥ 30). The stratigraphic sequence of the Madison formation has been described by several authors (Sonnenfeld; 1996, Buoniconti; 2008 and Thyne et al., 2010). These works concluded that the Madison is bounded by an angular unconformity at the bottom and a regionally karsted disconformity at the top. The Madison itself is subdivided into six third-order depositional sequences as shown in the wireline logs in Figure 5-2. These sequences are populated with the different facies that possess their own porosity and permeability. It can be observed from Fig. 5-2 that stratigraphic intervals can be correlated across the structure. The continuity of the stratigraphic sequences is confirmed by the observation of these sequences in outcrops in southwestern Wyoming (Sonnenfeld; 1996). This suggests that the reservoir is continuous and that lithology is consistent along the Arch. Logs indicate that the Madison is a generally continuous dolomite reservoir that contains very low porosity limestone beds. This indicates that there are no barriers to flow in the reservoir (continuous reservoir). Reservoir quality varies vertically and generally improves towards the top of the structure (Stilwell, 1989). Figure 5-2 shows that the highest porosity is found around the top of the transgressive system tract in sequence III (solid line).

Based on the porosity calculated from density and sonic Logs in Thyne et al., (2010), they observed a ‘tri-modal’ distribution. This porosity distribution indicates three petrophysical facies that can be correlated with the lithology and the depositional sequences across the formation. The samples have average porosity values of 2, 8 and 14%, respectively. The lateral variation in porosity is strongly dependent on the depositional facies and can be correlated over several kilometres across the structure (Thyne et al., 2010).

Over the productive gas bearing region of the structure, the reservoir closure is about 5,700 ft TVDSS and the gas/water contact is logged at 9,798 ft TVDSS (Figure 5-3(a)). More than fifty Paleozoic exploration wells on the Moxa Arch penetrated the Madison formation, with most of them on the north part of the Arch. Only two wells were drilled on the south of the anticline. From these exploration wells it was found that the average thickness of the reservoir
is 280 m, with the formation being thicker at the crest and gradually becomes thinner towards the south (from 250 m to 211 m, Becker and Lynds; 2012). The formation has an average porosity ranging between 10 to 14%, permeability is 10-50 mD and the irreducible water saturation is 10%.
Figure 5-2: Wire-line Logs correlating nine wells along the Moxa-Arch in the LaBarge Platform. The figure shows the six third order stratigraphic sequences within the Madison group that can be correlated across the structure. GR: gamma ray, MD: measured depth in feet and DPHI: core calibrated density derived porosity. (Thyne et al., 2010).
Figure 5-3: (a) Structure map for the Madison formation. Contour interval, 1000 ft. Dashed line indicates the GWC. (b) CO\textsubscript{2} composition map for the Madison formation. Contour interval, 5 percent. (Stilwell, 1989). CO\textsubscript{2} contour map generally matches the structure map, showing an increase in composition with depth.

5.1.1 Other Reservoir Properties

5.1.1.1 Pressure Gradient Data

Initial bottom-hole pressure readings obtained from drill stem tests before ExxonMobil started production in the Madison are shown in Figure 5-4. The pressure gradient in the gas leg suggests that the Madison is normally pressured, as the static reservoir pressure increases predictably (vertical equilibrium) across the structure with depth of the completion. This may indicate lateral continuity of the reservoir but does not mean the whole of the structure is fully productive (Stilwell, 1989). As explained earlier, the majority of the reservoir is of good
quality but some lateral barriers and baffles are present in the reservoir in the low porosity limestone and anhydrite beds. The reservoir pressure has also been measured in the water leg and the aquifer appears to be normally pressured as well. Extension of the pressure gradients in the gas and water leg intersect at 9678 ft TVDSS, which is slightly higher than that recorded by wire-line logs (9,798 ft TVDSS). Becker and Lynds (2012) attributed this to a non-linear function of pressure with depth in the gas leg and the gas compressibility of the thick gas column.

Figure 5-4: Original pressure measurements in the Madison formation (Becker and Lynds; 2012).

5.1.1.2 Archies Law Exponents

In the previous chapters, we assumed that the hydrocarbon fluids occupy the whole volume of the reservoir. In reality this is not the case. Hydrocarbon reservoirs are usually partially water saturated. The diffusivity is further reduced as the volume available for the fluid to diffuse is reduced and thus the tortuosity increases. We shall include a saturation dependency on the tortuosity term in Eq. 2-6 using a similar equation to Hu and Wang (2003). The effective diffusivity in the porous media is thus defined by:
The reader is reminded that $a$, $m$ and $n$ represent the tortuosity factor, cementation factor and the saturation exponent, all of which are present in Archie’s law (Archie 1942) and $S_{w}^*$ is the irreducible water saturation.

Values of the cementation factor ($m$) and tortuosity factor ($a$) are listed in Carothers (1968) and Traugott (1970) for different reservoir lithologies. The cementation factor ranges from 1.29 for sandstones to 3 for some carbonates and the tortuosity factor ranges from 0.62 in unconsolidated sands to 2.45 in Pliocene sands (Porter and Carothers, 1970). The saturation exponent ($n$) may vary between 2 for water wet rocks to 8 for oil wet rocks (Anderson 1986; Kumar et al., 2010). For the carbonate reservoirs such as the Madison formation, values of 0.85 and 2 are usually used for $a$ and $m$, respectively (Asquith and Krygowsky, 2004). While the value of $n$ is set to 2 (Anderson, 1986). With an average porosity of 14% and the irreducible water saturation of 0.1 of the Madison, these values combined will reduce the diffusivity by a factor of 0.13.

5.1.2 Reservoir Composition Gradient

The unusual gas composition and distribution of the Madison limestone formation, as it is composed mainly of non-hydrocarbons (approximately 80%), has made it the subject of several studies (Stilwell 1989 and Huang et al., 2007). Within the Exxon-Mobil operated unit (the LaBarge Field), it averages 66% of CO$_2$, 7% of Nitrogen (N$_2$), 5% of Hydrogen Sulphide(H$_2$S), 1% of Helium (He) and 21% of methane which is the only hydrocarbon. The composition of the gas samples analysed from the drill stem tests indicates a highly segregated system. The two main constituents of the gas are CH$_4$ and CO$_2$. The former varies from 23% at the crest of the Madison to 5% at the GWC, while the latter varies from 66% at the crest of the structure to 90% at the GWC. In the Madison reservoir on the northern part of the Arch (LaBarge Field), CH$_4$ composition varies with well locations on the structure (see Fig 5-5). Figure 5-3(b) shows the CO$_2$ composition contour map in the LaBarge Field. This map generally matches the Madison structure contour map, showing that CO$_2$ content increases with depth.
Figure 5-5: Current methane composition profile observed in the LaBarge Field; CH\(_4\) varies from 5% at the GWC to 23% at the crest. Adapted from Huang et al., 2007.

Huang et al., (2007 and 2011) previously touched on the reason (the flux) behind the segregated compositional gradient in this field. They proposed that gravity segregation alone cannot lead to the observed LaBarge profile. Using the fluid mixing tool MPATH to study different reservoir charging and mixing scenarios, they came up with a hypothesis that the trap was charged with two different fluids in the Laramide Orogeny (45 – 66 million years ago, Ma). The first fluid was almost pure CO\(_2\) (90%) while the second one was methane rich with a significant amount of CO\(_2\) (40%), and subsequent mixing via molecular diffusion led to the current compositional profile. The timescales found in this work is contemporaneous with volcano activity in west-central Montana which resulted in plutonic rocks in the Little Belt and Big Belt Mountains. They thus proposed that the CO\(_2\) rich fluid originated from mantle sources, perhaps associated with magmas were transported along the Wind River Thrust adjacent to the Wind River Mountain (Fig. 5-1). Late stage movement of this thrust occurred at the same time as the west-central Montana volcanoes. This work however focused on the management of the field and the surface facilities (acid gas injection plant) over production time scales, they did not disclose any information on the methods or parameters (such as the molecular diffusion coefficient) used in their work.
Luo (2009) also tried to reproduce the current methane distribution using MPATH. In this work, the structure was charged with two fluids; pure CO\textsubscript{2} and pure CH\textsubscript{4} and different sequences were investigated to see which reproduced the methane profile observed in the LaBarge. They obtained a ‘reasonable’ match when the system was initially filled with CO\textsubscript{2} and then charged with CH\textsubscript{4} for 20,000 years. Subsequent mixing via molecular diffusion for 800,000 years produced a CH\textsubscript{4} profile similar that observed in the LaBarge Field. However, this work is very simplified as most parameters (temperature, pressure, porosity and permeability) were assumed to be uniform in the reservoir. Order of magnitude estimates were also used to calculate the molecular diffusion coefficient which is the most important parameter in the mixing process. Evidence suggests that the gas accumulated in the Madison since the Eocene era; this work does not shed light on why the composition has remained the same after 800,000 years of mixing.

In the work by De Bruin (2001) and Stilwell (1989), the authors proposed a similar hypothesis to that of Huang et al., (2007). They hypothesized that the formation was initially filled with a methane rich fluid in Laramide-Oregeny (50 million years ago, Ma). However the increase CO\textsubscript{2} content in the Madison formation was attributed to the generation and migration of CO\textsubscript{2} rich fluid a lot later from Quaternary volcano activity (approximately 3 Ma) that occurred in the Rock Springs Uplift (Leucite Hills volcanic field) to the paleozoic reservoirs in the Greater Green River Basin. Well testing the Madison on the Rocky Springs Uplift have recovered some CO\textsubscript{2} rich gas, indicating that the volcanic may be capable source of CO\textsubscript{2}.

The differences in the mixing timescales in the works described above; Lou (2009), Huang et al., (2007 and 2011) and Stilwell (1989) is the basis of this work. The first two studies were done in-house and their findings have either not been published or are only vaguely described in presentations. They also only investigated the impact of the compositional mixing by molecular diffusion. The hypothesis proposed by Stilwell (1989) was not confirmed by any analysis. In the next sections, we shall use the models introduced in chapters 3 and 4 to investigate the impact of diffusion (pressure, molecular and thermal) and convection on the compositional profiles and thermodynamic timescales on the fluid in the LaBarge Field. The

\footnote{Confidential presentation of Hongjun of BP, Exploration & Production Technology}
main aim of this exercise is to find out the timescales at which the LaBarge was charged with its fluid.

### 5.2 1D Analysis

As CMG STARS® does not model the effect of thermal and pressure diffusion, we initially use the 1D diffusion code to carry out a simple investigation of the impact of these fluxes (and molecular diffusion) on the mixing of the fluids in the LaBarge and the timescales required for thermodynamic equilibrium.

<table>
<thead>
<tr>
<th>Component</th>
<th>CH₄</th>
<th>CO₂</th>
<th>H₂S</th>
<th>N₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molar mass (kg.mol⁻¹)</td>
<td>16.04 × 10⁻³</td>
<td>44.20 × 10⁻³</td>
<td>34.08 × 10⁻³</td>
<td>28.01 × 10⁻³</td>
</tr>
<tr>
<td>Molar volume (m³.mol⁻¹)</td>
<td>0.867 × 10⁻⁴</td>
<td>0.645 × 10⁻⁴</td>
<td>0.518 × 10⁻⁴</td>
<td>0.970 × 10⁻⁴</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
<td>0.025</td>
<td>0.058</td>
<td>0.083</td>
<td>0.031</td>
</tr>
</tbody>
</table>

The 1D numerical solution was derived to study the impact of the diffusion on fluid mixing in simple vertical systems. To use this for a complex structure like that in the LaBarge Field, we have to make some adjustments to the vertical dimension and force due to gravity in the program. In order to represent the Madison trap in one dimension, we assume the carbonate ramp deposit is a simple symmetrical dome-like structure. This would lead to the mixing process occurring at the same rate down both sides of the dome. We can therefore study the separation-mixing process of the structure using just ‘one side’. The Madison formation can be thus represented in its simplest form as an inclined rectangle. As we can see in the contour map (Fig. 5-3(a)), the Madison is not symmetrical; it spans an area of about 34 km by 102 km. Hence, we carry out two separate analyses using the shortest (20 km) and longest (41 km) distance from the crest of the structure to the GWC (represented by the red lines in Fig. 5-3(a)), to give the limits for the timescales for the separation-mixing process in this structure. In order to compare the CH₄ compositional profiles obtained from these simulations to that observed in the LaBarge (Fig. 5-5), the 1D model has to have a maximum...
height difference from the GWC to the reservoir crest of 1200 m. This is achieved by inclining the system by 1.6° and 3.4°, for the distances of 41 km and 20 km, respectively. The inclination of the 1D system will transform the acceleration due to gravity term to $g \sin \theta$, where $\theta$ is the angle of inclination to the x-axis.

For this initial exercise, we simulate an ideal binary mixture of the two main components in the LaBarge field; CH$_4$ and CO$_2$ under isobaric and isothermal conditions (under the influence of pressure and molecular diffusion alone). We carried out this study to investigate which diffusion flux is dominant in producing the observed LaBarge profile and will independently assess later on the impact of thermal gradients. The reader is reminded that there are no sources or sinks in our system (the number of moles are conserved). Thus as long as the average distribution of moles is the same and conserved through out the simulation, different initial conditions would give the same steady state solution. From the composition profile observed in the LaBarge (Fig. 5-5), we find the average of methane molar fraction ($\bar{x}_{CH_4}$) in the system to be 0.14 using the trapezium rule. To initialize our numerical model, we chose case 2 (section 3.2.2) where pure CH$_4$ is completely separated from pure CO$_2$. Based on Eq. 3-27 (see Appendix A2 for a more detailed solution), the pure CH$_4$ has to initially occupy the top 18% of the 1D domain in order to obtain a $\bar{x}_{CH_4}$ value of 0.14. The system described above is simulated at the initial pressure and bottom hole temperature measured in Mobil’s discovery well (44.8 Mpa and 410 K). Table 5.1 lists the properties of the pure components of the fluids obtained from REFPROP 8.0 (Lemmon et al., 2007) at these conditions.
Figure 5-6: (a) Change in CH4 compositional profile with time until steady state is attained. (b) After 620 Myrs the currently observed LaBarge profile is reproduced by the numerical simulation.

This analysis was performed using 51 grid points. The reader is reminded that this number of grids were found to be sufficient to model the 1D diffusion process in section 3.4. Figure 5-6(a), shows how the methane composition in the system changes with time under the influence of gravity and pressure diffusion. We observe that the initially segregated system becomes almost completely uniform after about 5050 million years (steady state) for the system modelled using the longer horizontal distance. This timescale is greater than the age of the earth, thus suggesting that the fluid in the Madison are still undergoing mixing and steady state has not be attained. This however is not the case as we explain later.

The separation of methane which is defined as the difference in mole-fraction of CH₄ at the top and bottom of the reservoir (Eq. 3-29), changes from 1 at initial conditions to 0.0169 (methane varies form 0.127 at the bottom to 0.144 at top of the domain) at steady state. This is expected as molecular diffusion tends to homogenize a mixture. This result suggests that the current CH₄ compositional profile observed in the LaBarge Field is one of a fluid mixture that has not reached thermodynamic equilibrium and mixing via molecular diffusion is still on-going. However, if we analyse the transient profiles from our simulation, we notice that at about 620 Myrs, we observe a similar compositional profile to that observed in the LaBarge (see Fig. 5-6(b)). The CH₄ composition varies from 0.234 to 0.050 at this timescale. This analysis was also done for the shorter areal dimension (20 km). In this case the mixing
timescales are reduced; it takes the system 145 Myrs and 1100 Myrs to reproduce the LaBarge compositional profile and reach equilibrium, respectively.

The timescales required to reproduce the LaBarge profiles obtained from the above analyses, 620 Myrs and 145 Myrs (for the horizontal lengths of 41 km and 20 km, respectively) are an order of magnitude larger than the time it was believed the LaBarge structure was originally charged (Laramide orogeny: about 50 Myrs), making them infeasible. The LaBarge timescales for the longer horizontal length is also higher than the time the Madison depositional episode terminated (about 300 Myrs). This is not possible as the rocks have not even been deposited at this time.

5.2.1 Impact of non-ideality

In sections 3.5.3 and 3.5.4, we highlighted the importance of modelling the non-ideality of fluids as this affects both the equilibrium composition and the timescales. The reader is reminded that in the 1D diffusion numerical solution, that the non-ideality of the mixture is modelled by the thermodynamic factor and for a binary ideal system this parameter is a scalar which equals to one. To investigate the impact of the non-ideality of the CH$_4$ and CO$_2$ mixture, we calculate the thermodynamic factor using the fugacity coefficients obtained from the Peng Robinson EOS. Fig. 5-7(a) shows the plot of the thermodynamic factor against the mole fraction of CH$_4$ in the binary mixture at 410 K and 44.8 Mpa. From this plot, we can see that this binary mixture can be treated as an ideal mixture; the thermodynamic factor is approximately one for all compositions. This finding is backed by the comparison of the CH$_4$ steady state profiles produced by the numerical solutions for both the ideal and real mixture cases (Fig 5-7(b)). We observe that the steady state profiles for the two cases overlap; the change in CH$_4$ separation is negligible (0.0169 in the case were the fluid is modelled as ideal and 0.0172 in the real case).

The change in the mixing timescales is also negligible when you compare the two cases. It takes the real system 660 Myrs and 5100 Myrs for the longer areal distance (41 km) and 157 Myrs and 1190 Myrs for the shorter distance (20 km) to reproduce the current LaBarge compositional profile and to attain thermodynamic equilibrium, respectively. As mentioned earlier, the LaBarge structure was originally filled approximately 50 Myrs ago. This and the
fact the shorter timescale (157 Ma) corresponds to the time it is believed the shales of Phosphoria (the source rock) just started generating hydrocarbons make the LaBarge timescales from these analyses infeasible.

Figure 5-7: (a) Comparison of the thermodynamic factor of the CH$_4$/CO$_2$ mixture produced for ideal and real cases. We conclude that this mixture can be assumed to be ideal. (b) Comparison of the CH$_4$ steady state compositional profile for the ideal and real cases.

Table 5-2: Summary of results obtained from the numerical simulations of pressure and molecular diffusion on the CH$_4$/CO$_2$ mixture for different initial compositions ($L = 41$ km).

<table>
<thead>
<tr>
<th>Case</th>
<th>$x_{CH_4}^{Top}$</th>
<th>$x_{CH_4}^{Bottom}$</th>
<th>$x_{CH_4}^{Diff}$</th>
<th>Equilibrium Time (Myrs)</th>
<th>LaBarge Time (Myrs)</th>
<th>Equilibrium Segregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>5100</td>
<td>660</td>
<td>0.0172</td>
</tr>
<tr>
<td>2</td>
<td>0.92</td>
<td>0.010</td>
<td>0.910</td>
<td>5000</td>
<td>600</td>
<td>0.0173</td>
</tr>
<tr>
<td>3</td>
<td>0.84</td>
<td>0.020</td>
<td>0.820</td>
<td>4900</td>
<td>570</td>
<td>0.0173</td>
</tr>
<tr>
<td>4</td>
<td>0.70</td>
<td>0.040</td>
<td>0.660</td>
<td>4770</td>
<td>480</td>
<td>0.0174</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.054</td>
<td>0.546</td>
<td>4680</td>
<td>405</td>
<td>0.0174</td>
</tr>
</tbody>
</table>
Table 5-3: Summary of results obtained from the numerical simulations of pressure and molecular diffusion on the CH$_4$/CO$_2$ mixture for different initial compositions ($L = 20$ km).

<table>
<thead>
<tr>
<th>Case</th>
<th>$x_{CH_4}^{Top}$</th>
<th>$x_{CH_4}^{Bottom}$</th>
<th>$x_{CH_4}^{Diff}$</th>
<th>Equilibrium time (Myrs)</th>
<th>LaBarge Time (Myrs)</th>
<th>Equilibrium Segregation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>1190</td>
<td>157</td>
<td>0.0173</td>
</tr>
<tr>
<td>2</td>
<td>0.92</td>
<td>0.01</td>
<td>0.91</td>
<td>1181</td>
<td>143</td>
<td>0.0171</td>
</tr>
<tr>
<td>3</td>
<td>0.84</td>
<td>0.02</td>
<td>0.82</td>
<td>1169</td>
<td>136</td>
<td>0.0174</td>
</tr>
<tr>
<td>4</td>
<td>0.70</td>
<td>0.04</td>
<td>0.73</td>
<td>1143</td>
<td>118</td>
<td>0.0172</td>
</tr>
<tr>
<td>5</td>
<td>0.60</td>
<td>0.054</td>
<td>0.546</td>
<td>1111</td>
<td>88</td>
<td>0.0173</td>
</tr>
</tbody>
</table>

5.2.2 Impact of Different Initial Compositions

As there is no clear understanding of the charge sequence or the exact composition of the fluids that charged the LaBarge, we studied other possible binary systems where the two initially segregated fluids contained both CH$_4$ and CO$_2$. Initializing the system with mixtures as opposed to using pure fluids will lead to a reduction in the initial composition gradient; which is the driving force for molecular diffusion. The initial rate of mixing for the diffusion process decreases with the lower initial composition difference. However a lower initial composition difference would mean less reduction in compositional difference to reach steady state. We investigated if the reduction of initial composition will give more reasonable LaBarge timescales.

We simulated several binary mixture systems in which the initial composition difference ranged from 1 (completely segregated system of pure CH$_4$ and CO$_2$) to 0.58; almost half of that in the previous study. In all the cases the CH$_4$-rich fluid is initialized above the CO$_2$ rich mixture and occupies the top 18% of the 1D domain. The initial composition of the mixtures are chosen using Eq. 3-27 so that all systems have the same number of moles ($\overline{x}_{CH_4} = 0.14$), thus all the systems attain the same steady state. Table 5-2 and 5-3, summarise the results obtained from this analysis. We observe that the changes in the mixing timescales are relatively small compared to the significant change in the initial composition difference. This is due to higher initial mixing rate in the systems with the higher composition difference. The
timescales required to reproduce the LaBarge profile is however almost halved. Table 5-3 shows the results of the analysis using the shorter distance (20 km); Case 5 gives timescales with the same other of magnitude (approximately 90 Myrs) to that of Huang et al., (2007). They were able to reproduce the LaBarge timescales after 50 Myrs of mixing using fluids approximately similar initial composition difference (one fluid was CH$_4$ rich with 40% of CO$_2$, while the other had 90% of CO$_2$). However, we could not directly compare our result to theirs as they did not disclose the exact composition of the mixture and parameters used in their work.

This timescale however does not correspond to any volcanic activity in the Greater Green River Basin; it is still 40 Myrs before the magmatic episode occurred in west-central Montana. Hence we cannot justify a source for the increase in CO$_2$ at this time. The timescales obtained from the analysis using the longer horizontal distance (41 km) are not feasible. Even the shortest mixing timescales (Case 5) occurs before the Madison formation was deposited.

5.2.3 Impact of Assuming Constant Reservoir Conditions

From the formulation of the diffusion coefficient, we observe that this parameter is dependent of composition, temperature and pressure. So far in our study on the LaBarge, we have calculated the diffusion coefficient assuming isobaric and isothermal conditions at 44.8 Mpa and 410 K. Under normal geothermal gradient (-0.03 Km$^{-1}$) and vertical equilibrium ($P = \rho gh$) the temperature and pressure in this formation will vary significantly with depth. In this section, we shall investigate the impact of the temperature and thermal gradient has on the mixing timescales.

For this exercise, we simulate the impact of molecular and pressure diffusion on only ‘Case 1’ of the shorter horizontal length (see Table 5.3). We ran two different cases:

- Variable reservoir conditions: the reservoir is initialized with a temperature and pressure gradient and the diffusivity is calculated at the different conditions of each grid point.
• Constant reservoir conditions: the molecular diffusion coefficient is calculated assuming isobaric and isothermal conditions (only dependent on composition).

![Diagram](image.png)

**Figure 5-8:** Comparison of the change in methane composition with time for the 6th grid. (o) represent simulation carried out at isobaric and isothermal conditions while the dotted lines represent the case with pressure and temperature gradients.

Figure 5-8 shows how methane composition of the 6th grid point \((z = -1176 \text{ m})\) changes with time until steady state is attained. We observe that the two curves overlap and both cases reach steady state at similar timescales (at 1190 Myrs and 1198 Myrs for the case with isothermal and isobaric conditions and variable reservoir conditions, respectively). From this analysis we can conclude that the temperature and pressure distribution in the Madison formation does not affect the timescales and the diffusion coefficient can thus be calculated at constant reservoir conditions, making our previous results valid.

In Appendix A6, we show that the dependence of diffusivity on composition is also negligible. We can thus conclude that although molecular diffusion coefficients are dependent on composition, temperature and pressure a good first approximation is to calculate this parameter assuming constant conditions.
5.2.4 Impact of Thermo-Diffusion

In section 3.5.2, we demonstrated the importance of modelling thermal diffusion. This diffusive flux can be of the same order of magnitude as that of molecular diffusion, thus enhancing or hindering the mixing process. It is therefore important to investigate the impact of this flux on the composition and timescales of the LaBarge fluids. In the exercises conducted thus far on the LaBarge field, we have simulated the reservoir under isothermal conditions.

The United States Geological Survey characterized and evaluated the undiscovered oil and gas resources in the southwestern Wyoming Province (SWWP), and constructed a geothermal gradient map for the area around Greater Green River Basin using about 4,300 bottom hole temperature measurements collected from about 3,300 geophysical log headers from oil and gas exploration wells. From the geothermal map (see Appendix A8), we find out that the LaBarge Field has a thermal gradient similar that found in normal reservoirs (30°C per 1 km). To investigate the impact of thermal diffusion, we modelled this geothermal gradient along with the thermal diffusion ratio of 0.6. Shukla and Firoozabadi (1988) found for this value for a CH₄ and CO₂ mixture at conditions similar to that in the LaBarge. The reader is reminded that a positive value of the thermal diffusion ratio means that the CH₄ migrates to the hot region, the bottom of the system.

![Graph showing CH₄ composition profile](image)

**Figure 5-9:** Comparison of the CH₄ compositional profile at steady state for the isothermal and non-isothermal cases.
Figure 5-9 compares the steady state CH$_4$ composition profiles for the isothermal and non-isothermal systems (including thermal diffusion) using ‘Case 1’ for the longer horizontal distance (41 km) as described in Tables 5-2. We observe that the CH$_4$ segregation has decreased slightly due to thermal diffusion (from 0.0172 in non-isothermal case to 0.012 in the case where thermal diffusion was implemented). This is due to the thermal diffusion flux opposing that of molecular diffusion; CH$_4$ is enriched at the bottom. However as the magnitude of the thermal diffusion flux is very small (compared to the molecular diffusion), the change in the steady state segregation is insignificant. There is also a negligible change in the mixing timescales when thermal diffusion is implemented; it takes 730 Myrs and 5300 Myrs to reproduce the LaBarge profile and steady state respectively.

The thermal diffusion ratio chosen from Shukla and Firoozabadi., (1998) was computed for an equi-molar mixture of CH$_4$ and CO$_2$. However in our case the average mole fraction of CH$_4$ is 0.14. The thermal ratio is dependent on composition and thus will differ at this composition. In order to test the uncertainty of the thermal ratio used, we ran another case with double the thermal diffusion ratio (1.2). We found that there was also negligible change in the steady state composition (see Fig. 5-9) and timescales (710 to reach LaBarge profile and 5480 to attain steady state). We can thus conclude that assuming the present thermal gradient in the LaBarge field has stayed the same since the field was charged, thermal diffusion is not a dominant flux in determining the steady state and timescales. These timescales are, however, infeasible as explained earlier.

5.2.5 Impact of Other Components

Interaction effects in the diffusion process may occur when ternary or multi-component mixture systems are modelled. In section 3.5.3, it was demonstrated how this affected the timescales and the steady state composition of the mixtures studied in Ratulowski et al., (2003) experiments. We thus investigated the impact of the other components present in the LaBarge gas (N$_2$ and H$_2$S) on the molecular diffusion and pressure diffusion process. Introducing these new components may also affect the non-ideality of the fluids.

In this investigation, we maintain that the LaBarge was charged by two different fluids (one CH$_4$ rich and the other CO$_2$ rich) and subsequent mixing via diffusion produces the current profile. In order to initialize the 1D domain with a quaternary mixture we used the average
gas composition of the Exxon-Mobil operated units in the LaBarge Field to determine the
initial composition of the segregated fluids. Normalizing these compositions and using Eq.3-
27 we find that the CH4 rich mixture which occupies the top 33% of the 1D domain has a
composition of 0.433, 0.386, 0.099 and 0.081 of CH4, CO2, H2S and N2, respectively. While
the CO2 rich fluid contains 0.005, 0.900, 0.03 and 0.065 of CH4, CO2, H2S and N2,
respectively. This will produce an average distribution of composition of 0.14, 0.74, 0.05 and
0.07 for CH4, CO2, H2S and N2. We simulate this system under both ideal and real conditions
using the longer of the horizontal distance (41 km).

Figure 5-10 shows the steady state composition profiles for each of the components. The
results are similar to those for the binary mixture case, as the diffusion process leads to an
almost uniform mixture. The CH4 segregation at steady state for the ideal and real cases is
found to be 0.0168 and 0.0174, respectively. The timescales from these simulations are also
similar to those found for the binary mixture system; it takes the case where the fluid is
assumed to be ideal 670 Myrs and 5200 Myrs and the real case 740 Myrs and 5600 Myrs to
produce the LaBarge CH4 profile and reach steady state, respectively. From Figure 5-10, we
can also conclude that the quaternary mixture can be assumed to be ideal as there is
negligible change in the steady state composition in the ideal and real systems. This finding
is backed up by the thermodynamic factor matrix values of the quaternary system which are
summarized in Appendix A9. The diagonal terms are close to one and off-diagonal terms
values are close to zero; this is characteristic of an ideal mixture.
Figure 5-10: Comparison of the species steady state composition profiles produced for a quaternary mixture of CH$_4$/CO$_2$/H$_2$S/N$_2$ for the ideal and real cases.

Figure 5-11 investigates whether interaction effects become present when the quaternary fluid mixture is modelled. The molecular diffusion flux for species $i$, $J_i^M$ against the compositional gradient $-\partial x_i/\partial z$ for the ideal and real mixture systems for the grid point $z = 3075$ for all the time-steps until steady state is attained. The sign convention of the x-axis value and the y-axis value of each point are the same throughout the simulation. This indicates that the mixture diffuses ‘normally’.
Figure 5-11: Molecular diffusion flux versus compositional gradient for the quaternary mixture for the ideal and real systems.
The steady state composition produced by the numerical solution can be confirmed using the new 1D analytical solution for the steady state compositional profile for fluids under the influence of molecular and pressure diffusion we derived in section 3.3.1. As explained previously this model outperforms previously derived analytical solutions as we do not require the steady state composition at a reference depth to calculate the remainder of the steady state compositional profile. It is shown in the previous section that thermal diffusion and the impact of the other components of the mixture have a negligible impact on fluid mixing; thus assuming a binary mixture using the current CH$_4$ profile to calculate the average distribution of this component in this field, we are able to calculate the steady state profile. The steady state profile is consistent with that obtained from our numerical simulations; reinforcing the fact that the LaBarge will be a uniform mixture at steady state under the influence of gravity and molecular diffusion (see Figure 5-12). If the analytical solution such as that of Firoozabadi (1999) were used on the current LaBarge profile, they would just replicate the observed profile as this field is not yet at steady state.

Figure 5-12: (a) Comparison of the CH$_4$ steady state profile produced by the numerical simulation (○) and the analytical solution (solid line). (b) Plot of the absolute deviation between the two methods.
5.3 2D Analysis

From the 1D simulations we conclude that the fluid mixture in the LaBarge field can be modelled correctly using just a two component ideal mixture of CH$_4$ and CO$_2$ as the quaternary mixture produces similar results to the binary case. The impact of thermal diffusion in this binary mixture has been proven to be negligible and molecular diffusion has been found to be the dominant diffusive flux in determining the mixing of the fluids. The LaBarge timescales obtained from the 1D simulations so far are however infeasible. We shall now increase the complexity of the modelling of the field to try and get a better agreement with the timescales.

The 1D numerical solutions does not take into account the thickness of the structure. Compared to the horizontal lengths and the elevation of the Madison formation, this structure is relatively thin (280 m). Nonetheless it might affect the mixing timescales of this system. In a 2D domain, bulk movement due to density gradients (convection) also occurs. In section 4.4.2 we demonstrated that the timescales of mixing are significantly reduced when convection is modelled alongside diffusion. We thus perform a 2D investigation of convection and molecular diffusion using CMG STARS® on the fluids in the LaBarge Field. The properties of the reservoir used in the simulation are summarised in Table 5.4.

<table>
<thead>
<tr>
<th>Table 5-4: Reservoir properties for CMG STARS® 2D simulations.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grid</td>
</tr>
<tr>
<td>Dimensions</td>
</tr>
<tr>
<td>Porosity</td>
</tr>
<tr>
<td>Permeability</td>
</tr>
<tr>
<td>Datum Temperature</td>
</tr>
<tr>
<td>Datum Pressure</td>
</tr>
<tr>
<td>Temperature gradients</td>
</tr>
<tr>
<td>Diffusion Coefficient</td>
</tr>
</tbody>
</table>
The 2D inclined system is initialized in a similar way to the 1D analysis (case 1), with a pure CH$_4$ mixture occupying the top 18% of the domain, while pure CO$_2$ occupies the remainder. To obtain the correct reference pressure required to initialize the CMG STARS® model (using the vertical depth averaging method), we checked the steady pressure gradients in our model against the initial preproduction pressures produced observed in the Madison formation (Fig. 5-4). We found that using a reference pressure of 41 MPa at the top of the structure resulted in a pressure gradient similar to that observed in the field when the simulator had produced the same CH$_4$ profile observed in the LaBarge (Fig. 5-13).

\[
y = 0.1834x - 7925.2 \\
R^2 = 0.9441
\]

\[
y = 0.1843x - 7939.4 \\
R^2 = 0.9996
\]

Figure 5-13: Comparison of the observed pressure gradient in the Madison from the DST to the that in the CMG STARS® simulations (L = 20 km).

Fig. 5-14 shows the methane distribution in the system after 3000 years. Density driven natural convection has occurred very quickly leading to the interface tilting from its original vertical position till it is flat. Subsequent mixing via molecular diffusion then occurs. Figure 5-15 compares the mixing timescales for the two horizontal distances; this plot shows how the separation metric of CH$_4$ (defined by Eq. 4-15) changes with time until thermodynamic equilibrium is attained. The separation of methane changes from 0.98 at initial conditions to 0.0161, similar to that found in the 1D simulation (0.0169). However the timescales have been significantly reduced by over two orders of magnitude compared to the 1D simulations; the 2D system reproduces the current LaBarge CH$_4$ profile (CH$_4$ separation of 0.184) and attains steady state at 4 Myrs and 110 Myrs respectively for the reservoir length of 20 km.
We describe steady state in this exercise at the point where the CH$_4$ separation metric has reduced to $1 \times 10^{-2}$ in order to reduce computational time. The same analysis was performed using the horizontal dimension (41 km) and the methane profile currently observed in the LaBarge was reproduced at 9 Myrs. It will also take a lot longer to attain steady state in this simulation due to longer distance. As this is not the main focus of our work we ran this case only for 100 Myrs. From Figure 5.15(a), we observe that at this timescale the CH$_4$ separation metric is an order of magnitude greater than that at steady state. It is also observed that the rate of mixing at later time is relatively slow due to the reduced compositional gradient. From this pattern we can estimate the steady state timescale to be approximately 500 Myrs. This significant decrease in the mixing timescales is attributed to modelling the thickness of the Madison formation as this increases the area over which diffusion occurs.

The timescales obtained from the 2D simulations required to reproduce the methane profile observed in the LaBarge field are an order of magnitude less than that found in the work by Huang et al., (2007). The reader is reminded that they proposed that the reservoir was filled about 50 Ma by two sources, with one CH$_4$ rich and the other mainly composed of CO$_2$ which originated from volcanic activity in west central Montana. Assuming this hypothesis, our simulations indicate that the fluid should be more mixed than the current state observed in this field (a relatively more uniform methane composition should be observed in the field as the reservoir is not compartmentalized). The timescales obtained are however closer to that proposed in the works by De Bruin (2001) and Stilwell (1989) who hypothesized that the Madison was initially filled from the shales of the Phosphoria about 50 Myrs and later on enriched with CO$_2$ from quaternary-tertiary volcanic activity (approximately 3 million years ago). Thus subsequent mixing by molecular diffusion for approximately 3 Myrs will reproduce the observed LaBarge profile. To obtain a more definite mixing timescale for the LaBarge field, we shall now perform a study to see how the 3D structure affects the fluid mixing.
Figure 5-14: Methane distribution in the 2D inclined domain.

Figure 5-15: (a) Plot showing the change in methane separation metric with time for the two different areal dimensions. (b) In the case of the smaller distance (20 km), the observed methane profile in the LaBarge is produced after 4 Myrs of fluid mixing.
5.4 Impact of the 3D Structure

Most studies (Ghorayeb and Firoozabadi; 2000, Nasrabadi et al., 2006 and Nasrabadi and Firoozabadi; 2005) that investigate the compositional variations in hydrocarbon reservoirs have limited their analysis to the $x$-$z$ plane (2D). Hydrocarbon reservoirs are three dimensional (3D) structures and the 3D effect has been found to be particularly important in tilted reservoirs (Gardner et al., 1962). Here we investigate the impact of the shape and boundaries of the Madison formation on the mixing timescales. Based on the Madison structure map in Fig. 5-3(a) we built a three dimensional model using Petrel® with a total of $80 \times 100 \times 10$ grid blocks (42% of which are active). We chose to use this grid size after the grid refinement exercise described in Appendix A10. Figure 5-16 shows the IJ section (aerial view) of the 3D model. As we do not have wire line log and core data, we set the parameters such as permeability, porosities and formation thickness as uniform using the same values from the 2D exercise. This model was then exported to CMG STARS® and initialized with the lighter fluid; CH$_4$ on top of the heavier CO$_2$. To initialize the domain with the same amount of CH$_4$ as the previous cases, the structure is saturated with CH$_4$ at depths less than 2280 m. This was done in order to obtain a $\bar{x}_{CH_4}$ value of 0.14. Figure 5-17 shows the methane distribution in the structure changes from initial conditions till when the LaBarge profile is observed (3 Myrs).

![Figure 5-16: Aerial view of the 3D model of the Madison formation.](image-url)
Figure 5-17: Simulation results for the change in CH₄ content in the Madison formation with time. The currently observed CH₄ profile is reproduced after 3Myrs (c).

Figure 5-18: a) Plot showing the change in methane separation metric with time for early time. (b) Simulation results compared to the observed methane profile in the LaBarge after 3 Myrs of fluid mixing.
In the 3D exercise, we assume that the gravitational overturning process has occurred very quickly and initialize methane (the lighter component) on top of carbon dioxide. We are thus modelling the effect of molecular diffusion only. As we are mainly interested in the timescales to reproduce the observed CH$_4$ profile, we only ran this simulation for 5 Myrs. Figure 5.18 (a) shows the change of the CH$_4$ separation metric with time for this configuration compared to that of the 2D analysis. We observe that the initial mixing rates are higher in the 2D domains. However, at around 2 Myrs the rate of mixing in the 3D system overtakes that of the 2D systems as they slow down. We can thus extrapolate that the steady state timescales of the 3D system will be approximately 110 Myrs or less.

### 5.5 Discussion

From the result from the simple 3D model of the LaBarge, we propose a hypothesis similar to that of Stilwell (1989). We propose that the field was charged with a methane rich fluid early in the Laramide orogeny (approximately 50 Myrs ago) which underwent subsequent thermal degradation to give a methane rich gas that contained some CO$_2$. The structure was then enriched with a CO$_2$ rich fluid about 3 million years ago and subsequent mixing which is molecular diffusion dominated led to the current observed profile. Based on this compositional trend we propose that the CO$_2$ rich fluid originates from volcanic sources that occurred in the Pliostocene (approximately 3 Myrs). As mentioned earlier, De Bruin (2001) and Stilwell (1989) attributed the increase in CO$_2$ source to the Quaternary intrusive volcanic on the northern end of Rock Spring Uplift (Leucite Hills volcanic field, see Fig. 5-1). The volcanic activity that led to formation of the Leucite Hills is believed to have occurred from about 3.1 to 1 million years ago. The timescale found by our simulation is in this range. After CO$_2$ was generated they hypothesized it then migrated westward into the Moxa Arch structure.

We also conclude that non-equilibrated methane composition in the formation is due to incomplete mixing of the fluid. Wire-line logs (Thyne et al., 2010) show that the reservoir is a predominantly continuous dolomite structure; therefore modelling the reservoir with uniform properties (porosity and permeability) is a good initial assumption as we do not have access to the petro-physical data.
5.5.1 Comparison to Previous Studies

This timescale is four times bigger than that found by Lou’s analysis (2009). In his study a molecular diffusion coefficient which is similar to that we calculated using Leahy-Dios and Firoozabadi (2007) was used for the MPATH simulation \(1 \times 10^{-9} \text{ m}^2\text{s}^{-1}\). However there is a difference in the two LaBarge timescales (3 Ma from our work and 800,000 from Lou’s work). This difference is perhaps due to the difference in the approach used in the different works. As stated earlier, in Lou’s work he carried out an investigation to see what the charge sequence of the formation was by initially filling the structure with either pure CH\(_4\) or CO\(_2\) and then injecting the other component over a period of time. They obtained a ‘reasonable’ match when the system was initially filled with CO\(_2\) and then charged (injected) with CH\(_4\) for 20,000 years. Subsequent mixing via molecular diffusion for 800,000 years produced a CH\(_4\) profile similar that observed in the LaBarge Field.

We know from literature that Madison was initially sourced with a CH\(_4\) rich fluid, thus initially saturating the structure with pure CO\(_2\) is an infeasible hypothesis. This, however, was done because it was the only charge sequence that was able to lead to the CH\(_4\) the migrating to the top of the structure, above the CO\(_2\) (similar to the initial species distribution in our work); thus reproducing the LaBarge profile. The reduced mixing timescales could be attributed to the reservoir filling occurring simultaneously with the molecular diffusion process (molecular diffusion occurs whilst the structure is being injected with the CH\(_4\)).

The timescale is also an order of magnitude smaller than that found by Huang et al., (2007). In order to investigate the reason behind the larger mixing timescales in their work (50 Myrs), we carried out a sensitivity analysis on the tortuosity term in the diffusivity as most of the parameters used to simulate the fluid mixing process were not disclosed (they only stated the average porosity (8% to 10%) and irreducible water saturation values (0.1) in their paper). The reader is reminded that in porous media the diffusivity is restricted by the existence of a solid matrix. As the fluid can only move through the pore network, its effective diffusivity is reduced. This restriction is defined by the tortuosity. The tortuosity is dependent on \(\phi, S_w, a, m, n\) as defined by Eq. 5-1. Most of these parameters are obtained from borehole petrophysical data in the process of calculating the apparent water resistivity.
This process is plagued with uncertainties as data is obtained after screening of geophysical logs whose quality range from poor to excellent. We thus performed a sensitivity study to see what impact these uncertainties would have on the timescales of fluid mixing. For the simulations described in this chapter, we used an average porosity value of 0.14, which we obtained from the data presented at the Wyoming oil and gas field symposium and a $S_W$ value of 0.1 (from Huang et al., 2007). For the Archie exponents; $a$, $m$ and $n$ we used generic values for carbonate water wet reservoirs, 0.85, 2 and 2. Inputting all these values into Eq. 5-1 we obtain a tortuosity value of 0.13.

Keeping all the other parameters constant and changing only the average porosity value to that stated in Huang et al., (2007), we find that the tortuosity calculated by Eq.5-1 decreases to almost half of its original value (0.07). This will lead to a more restricted flow; thus the fluid mixing timescales will increase. This is however expected as the porosity is directly proportional to the tortuosity. Thus as in this case, 42% change in porosity will lead to 42% change in tortuosity. This analysis was done for other parameters (see Fig. 5-19) except for $S_W$ as this the same in both studies. We used a $m$ value of 2.46 for the sensitivity study. This was obtained from petrophysical data from the Red River Formation (MacCary, 1984). This formation was chosen as it has the same lithology as the Madison (dolomite and limestone) and is located south of the Moxa Arch. For the other two parameters, we used generally accepted values for water wet carbonates as we could not find the values for the Madison formation in literature (Peng et al., 2012; Ransom 1974).
From the tornado plot in Figure 5-19, we observe that the tortuosity is very sensitive to the changes in the parameters used for its calculation. It is most sensitive to the cementation factor \((m)\); changing this parameter from 2 to 2.46 leads to 60% increase in the restriction to flow. As these new selected parameters all fall in acceptable range for that of a carbonate reservoir such as the Madison formation, we ran a final simulation to see if the combined effect of these changes will give timescales similar to that found by Huang et al., (2007). From the tornado plot (Fig. 5-19), we can already see that this will have a significant effect on the tortuosity. It will decrease by two orders of magnitude (from 0.13 to 0.007). Fig. 5-20(a) shows how the methane separation metric changes with time for this case. We observe that the timescale required to reproduce the LaBarge profile has increased from 3Myrs in the initial case to approximately 30 Myrs. Giving the rather large decrease in the tortuosity value one will expect a bigger increase in the timescale. This however can be explained by the fact that molecular diffusional mixing occurs very quick initially as the compositional gradient is large. The steady state timescales will however be significantly larger as the compositional gradient is reduced.
The sensitivity analysis study shows how the timescales required to reproduce the observed LaBarge profile is very sensitive to small changes in the parameters used to calculate the tortuosity. This increased timescale is however still 20 Myrs smaller than that found by Huang et al., (2007). For our simulations we have assumed a uniform porosity distribution in the formation as we do not have any access to the wireline logs for this formation. However, as explained in section 5.1 the Madison is not completely homogenous; it constitutes of good quality dolomite inter-bedded with poorer quality limestone. Thyne et al., (2010) show that porosity distribution can be correlated in wells across the whole formation. Perhaps if we use good reservoir model that is populated with this porosity zones (from the logs) to carry out the study, the path which the fluid will have to diffuse through will be more tortuous. Thus the timescale will further increase, perhaps to approximately 50 Myrs.

Figure 5-20: Figures analysing the impact of increased tortuosity: a) Plot showing the change in methane separation metric with time till the observed LaBarge CH₄ separation metric is achieved for a more tortuous system (b) Simulation results compared to the observed methane profile in the LaBarge after 28 Myrs of fluid mixing.
5.6 Chapter Summary

There are several hypotheses in literature regarding the increased CO$_2$ composition in the Madison formation. De Bruin (2001) and Stilwell (1989) proposed that the formation was originally filled with a CH$_4$ rich mixture about 50 Ma, then later filled with CO$_2$ rich fluids associated with quaternary-tertiary magmas (3 Ma). Subsequent mixing by molecular diffusion should then reproduce the observed unusual gas distribution. Huang et al., (2007) on the other hand performed compositional data and fluid inclusion studies to explain this unusual gas distribution. From their results they proposed that the formation was charged with a CH$_4$ rich and CO$_2$ rich fluid at the same time, 50 Ma. This timescale is contemporaneous with volcanic activity around the west-central Montana. In house work by Lou (2009) also explained this unusual gas composition using MPATH. However, he was able to reproduce the observed CH$_4$ profile in this field after 800,000 years.

To test these various hypotheses, we investigated the impact of diffusion and natural convection on the unusual gas compositional gradients observed in the LaBarge field in the Madison formation. This low angle carbonate formation is located on the crestal position of the Moxa Arch in southwestern, Wyoming. We initially used the 1D diffusion numerical model described in Chapter 3 to analyse the impact of the diffusion (pressure, molecular and thermal) fluxes on the steady state composition and timescales. From this analysis, we found that impact of thermal diffusion is negligible and molecular diffusion is dominant in the fluid mixing of the LaBarge fluid. The steady state composition produced from this model suggests that the current LaBarge profile is one of incomplete mixing and a homogenous fluid will be obtained after mixing by molecular diffusion after several billions of years.

We also found that non-ideality and interaction effects play an insignificant part in the mixing of the LaBarge fluid. In the final section of this chapter, we built a simple reservoir model of the Madison formation and used CMG STARS® to simulate fluid mixing by molecular diffusion to determine the timescales that will reproduce the observed CH$_4$ profile. Our results backs the hypothesis by De Bruin (2001) and Stilwell (1989) who suggest the formation was initially filled 50 million years ago then charged with a CO$_2$ rich fluid 3 million years ago. Thus subsequent mixing by molecular diffusion for 3 million years will reproduce the current composition distribution in the field. This is in contrast to the results found by
Huang et al. (2007) who suggested that it will take 50 million years of mixing to reproduce the current CH$_4$ profile. However, we showed how sensitive the diffusion tortuosity is to the parameters used to calculate this term. A small acceptable increase in these parameters significantly increases the timescales. We thus propose that a good reservoir model that captures the porosity distribution in the field along with accurate bore hole petrophysical data is required to obtain a precise mixing timescale.
Chapter 6

Conclusions and Future Work

6.1 Conclusions

The research conducted in this thesis led to the following findings:

1. A one dimensional numerical model for multicomponent diffusion (molecular, pressure and thermal) in porous media was developed to gain further understanding of the fluxes that govern the compositional variation in single phase hydrocarbon reservoirs and the time required to reach thermodynamic equilibrium.

2. A new explicit analytic solution for steady state compositional profiles and separation for an ideal mixture under the influence of pressure and molecular diffusion was also developed. The advantage of this solution over previous versions is that the steady state composition at a reference point in the 1D domain is not needed to calculate the steady state compositions. The new analytical solution performs well and gives very consistent results with a maximum average absolute deviation (AAD) of 0.03 even when the density difference in the system is unrealistically large.

3. We found that thermal diffusion which has been omitted from a number of previous studies when modeling the diffusion mixing process can play a significant role in the diffusional mixing. This flux can enhance or weaken the steady state compositional profile as this flux can have the same order as the molecular diffusion flux.
4. The non-ideality and multicomponent diffusion interactive effects are the most important factors that determine the steady state composition and timescales in the two ternary mixtures \( nC_1/nC_5/nC_{11} \) and \( nC_1/nC_5/MNP \) studied in Ratulowski et al., (2003) experiments. Although the \( nC_{11} \) and MNP have similar molecular weight, their structure is very different which makes the later mixture more non-ideal and causes it to segregate 5.5 times more than the previous mixture.

5. Multicomponent molecular diffusion interactive effects in the \( nC_1/nC_5/MNP \) mixture lead to the reverse diffusion phenomenon occurring in this mixture. This doubles the timescale for thermodynamic equilibrium in this mixture when it is modelled as real compared to the ideal mixture.

6. Although molecular diffusion coefficients are dependent on composition, temperature and pressure, a good first approximation is to calculate them assuming constant conditions. The effect of this assumption on the mixing timescales is however negligible.

7. An investigation of the impact of density and thermal driven natural convection and molecular diffusion on fluid mixing in a 2D domain was conducted using CMG STARS®. Reservoir inclination and heterogeneity had the biggest effect on the fluid mixing dynamics, increasing the steady state timescales. Inclining the studied system by just \( 5^\circ \) causes the timescale to reach steady state to increase by a factor of 3.

8. The investigate the possible causes of the unusual gas distribution in the Madison formation we used the numerical model for 1D diffusional mixing and CMG STARS® to test various hypotheses. From the 1D results we found that the LaBarge mixture can be accurately modelled using a simple ideal binary mixture of methane and carbon dioxide as the thermodynamic factor of the fluid is similar to that of an ideal mixture. Also the inclusion of other components in the LaBarge (Hydrogen Sulphide and Nitrogen) had an insignificant effect on the steady state compositions and timescales.

9. Thermal diffusion is negligible for this system; unrealistic geothermal gradients are required to make this flux reverse the impact of molecular diffusion, which is the dominant diffusion flux.
10. Molecular diffusion would lead to a completely homogenized mixture in the LaBarge field. Thus the current LaBarge composition profile is one of a system that is not yet at equilibrium.

11. Our models suggest that approximately 3 million years of mixing via molecular diffusion has produced the current profile observed in this field. This timescale is contemporaneous with the quaternary-tertiary volcanic activity that occurred in the Rocky Spring Uplift that was proposed by De Bruin (2001) and Stilwell (1989).

12. We thus propose that this field was charged with two fluids; one predominantly CH₄ about 50 million years ago and the other CO₂ rich about 3 million years ago, then subsequent fluid mixing which is molecular diffusion dominated for 3 million years led to the currently observed LaBarge fluid distribution.

6.2 Recommendations for future work

The research conducted in this thesis could be extended in the following areas:

1. In this work we have only studied the impact of the diffusion and convection fluxes on single phase mixtures. This work can be extended to study two phase and three phase mixtures by including flash calculations and stability criterion checks in the 1D numerical model. Capillary effects can also be investigated.

2. We demonstrated the importance of modelling thermal diffusion. However, we used constant thermal diffusion ratios to implement this flux in the numerical model. Future work should incorporate correlations to calculate this parameter into the code as it is dependent on temperature, pressure and composition.

3. We studied the impact of natural convection and molecular diffusion without including thermal and pressure diffusion as CMG STARS® does not model these fluxes. This was mitigated by investigating the diffusional flux in the 1D numerical model. Developing a numerical model that incorporates all the fluxes and captures and model the complex structure of hydrocarbon reservoirs will advance this work.

4. We assumed a closed boundary for the reservoirs studied in this work. In reality there could be on-going reservoir filling or another reservoir might leak into the studied reservoir. These effects can be included into the numerical model by changing the
boundary conditions or including sources or sinks in the models (for example in the form of wells in the CMG STARS models).

5. We only considered homogenous reservoirs and systems with permeability layering. The model can be extend to include other forms of heterogenities such as faults and fractures.

6. In the LaBarge analysis, we built a simple reservoir model based on the structure map of the structure and assumed a uniform thickness. In reality this is not the case; the reservoir thins towards the south of the structure. We have also assumed that all reservoir properties apart from the temperature is uniform in our model. Future work should use accurate reservoir and geological model that truly captures the porosity, permeability and facies distribution observed in the wire-line logs and cores. This will have an adverse effect on the timescales.

7. We showed that the diffusion tortuosity is very sensitive to the parameters to the porosity and Archie exponents. A small acceptable increase in these parameters will significantly increase the timescales. In our work, we used Archie exponents from literature for a generic carbonate water wet reservoir to calculate the tortuosity. We propose that accurate bore hole petrophysical data for the Madison formation should be used in the future in order to calculate a precise timescale.

8. With a good geological model as explained earlier and integrating our model with basin modelling, we can provide a more comprehensive study of compositional variation in the LaBarge field.
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SCHLUMBERGER OILFIELD GLOSSARY 1998.


Appendices

A.1 Computer Program for 1D Pressure and Molecular Diffusion

In this section we describe the computer program we developed to numerically solve the diffusional fluid mixing problem (by molecular, pressure and thermal diffusion) in a one dimensional domain.

A.1.1 Program Description

The code was written in the C programming language and compiled with the Microsoft Visual Studio 2010 software. A third party matrix and vector linear algebra library called LAPACK was employed to efficiently implement matrix and vector manipulations and calculations on C. The C programming language uses libraries as its primary method of extension. A library is a set of functions contained in a single ‘archive’ file. Each library either built in or user defined has a header file where the functions are declared and a source file where the variables of functions are defined and the functions are implemented. Then all of this is brought together in a main source file; where all the libraries are called.

A.1.2 Flow Chart

Figure A-1 below shows the flow chart of the numerical solution for the diffusion process. This flow chart is the algorithm and a summary of the main functions implemented in the computer programs (which may have several sub-routines).
Initialization

Prompt user to choose what number of grids and initial composition distribution to be implemented. Initial $M \times N$ matrix of mole fractions is created. $M =$ number of components and $N =$ grid points.

Calculate Main Parameters

Create variables using parameters of certain mixtures from input file. These variables include: density, concentration.

Make $[B]^{-1}$

Uses the Stefan Maxwell coefficients to produce the matrix $[B]$ and then $[B]^{-1}$ at each node.

Is the fluid ideal?

Yes

Make $\Gamma$

Creates a $M \times M$ matrix of the thermodynamic factor.

No

Find $\Delta T$

Uses parameters and the CFL equation to find the time-step for all three diffusion processes. The lowest is chosen.

Diffusion Flux

Calculates the molecular, pressure and thermal diffusion flux and then implement the finite volume method to calculate the concentration at the next time step.

$C_i^t - C_i^{t+1} \leq 1e^{-5}$

Steady state achieved
A.1.3 Input Files

We use prompts from the terminal when the code is run to initialize the code. The user is prompted to choose what fluid mixture to study, whether the fluid mixture should be assumed to be ideal or real, the initial composition distribution, number of grid size and other reservoir properties.

A.1.4 Source Files

In this section we summarize the main source files implemented in our computer program.

- “main.c”: This is the source file where all the main functions are defined and called. The main objective of this is to file implements the finite volume method which advances the composition with time until steady state is attained.
- “algebra.c”: C programming language does not readily carry out matrix/vector calculations like MATLAB. We thus used this source file to implement well known algorithm for all matrix and vector manipulations and algebra.
- “inv.c”: This file utilizes the external third party matrix and vector linear algebra, LAPACK to calculate the inverse of a matrix. This is applied in the inverse of the Ficks diffusion coefficient which is then used in “main.c” to calculate the diffusion fluxes.
- Others (“peng.c”, “unifac.c” and “diff_s.c”): The first two source files contain the correlations for calculating the activity coefficient using the Peng-Robinson and UNIFAC Dortmund equation of state, respectively. While the last one implement the correlations to calculate diffusion coefficients.

A.1.4 Output Files

The computer program outputs the composition of each species at each grid point as it changes with time until steady state is achieved. In the implementation of the computer code the height of the reservoir is used to define the top and bottom of the 1D domain \((H = 2L)\). Thus the dimensions of the reservoir is confined to \(-L \leq h \leq L\). The output data is saved as
Microsoft Excel files (.xls). The first row denotes spatial coordinates. The subsequent columns indicate the mole-fractions at the specified grid point for a certain time step. An example of the output file is shown below. In this case \( H = 304.8 \) m.

<table>
<thead>
<tr>
<th>tstep</th>
<th>Years</th>
<th>dt</th>
<th>gp = 31</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>z \quad -152.4 \quad -142.24 \quad -132.08 \quad -121.92 \quad -111.76</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>10</td>
<td>0.3</td>
</tr>
<tr>
<td>1</td>
<td>74.57235</td>
<td>2.35E+09</td>
<td>0.300016</td>
</tr>
<tr>
<td>2</td>
<td>149.1447</td>
<td>2.35E+09</td>
<td>0.300026</td>
</tr>
<tr>
<td>3</td>
<td>223.717</td>
<td>2.35E+09</td>
<td>0.300031</td>
</tr>
</tbody>
</table>
A.2 Extended Derivation of the New Analytical Steady State Solution for the 1D pressure and Molecular Diffusion Process

For a reservoir of height 2L, where -L ≤ z ≤ L, the total number of moles of each component in the whole reservoir stays constant regardless of the composition profile at any time

\[ \int_{-L}^{L} c_i(z) \, dz = \int_{-L}^{L} c_i(-L) e^{-\frac{\rho_i dz - M_i (z + L)}{RT}} \, dz = \int_{-L}^{L} c_i^0 \, dz. \]  \hspace{1cm} (A2-1)

As density does not vary much along the reservoir, molar mass \( M_i \) is constant and at steady state the concentration along the reservoir does not vary that much. Therefore the above equation can be simplified taking \( c \) and \( \frac{RT}{(\rho_i - M_i)g} \) as approximately constant.

\[ \int_{-L}^{L} x_i^0 \, dz = \int_{-L}^{L} x_i(-L) e^{\frac{\rho_i dz - M_i (z + L)}{RT}} \, dz \approx \frac{x_i(-L)}{\theta_i} \left( e^{2\theta_i L} - 1 \right) \]  \hspace{1cm} (A2-2)

Where

\[ \theta_i = \frac{\rho_{\text{average}} v_i - M_i}{RT} g \]  \hspace{1cm} (A2-3)

Rearranging this equation yields,

\[ x_i(-L) \approx \frac{\theta_i \int_{-L}^{L} x_i^0 \, dz}{(e^{2\theta_i L} - 1)} \]  \hspace{1cm} (A2-4)

Thus we obtain a general expression for the steady-state mole-fraction of each component at every point in the reservoir

\[ x_i(z) \approx \frac{\theta_i \int_{-L}^{L} x_i^0 \, dz}{(e^{2\theta_i L} - 1)} e^{(z+L)\theta_i} \]  \hspace{1cm} (A2-5)
Besong (2010) derives this equation only for system with uniform initially condition. We shall now modify this equation to deal with the other two initial conditions.

### A.2.1 Uniform Concentration

This is the simplest case as initial mole fraction $x_i^0$ is constant throughout the reservoir. Therefore, we obtain

$$x_i(z) \approx \frac{\theta_i 2x_i^0 L}{e^{2\theta_i L} - 1} e^{(z+L)\theta_i}$$

(A2-6)

### A.2.2 Step Function like Concentration Distribution

In this case, the initial condition is not uniform, thus $x_i^0$ will be taken as the average distribution of the initial condition in space $x_i$.

![Figure A.2: Illustration of a Reservoir with a step function like initial concentration distribution](image)

Thus,

$$x_i = \frac{\int_{-L}^{L} cx_i(z)dz}{\int_{-L}^{0} cx_i(z)dz + \int_{0}^{L} cx_i(z)dz}$$

(A2-7)

This can be simplified by taking the summation of the volume each component occupies in the reservoir.
\[ x_A \approx \frac{\sum_{L} z c_A V_1}{\sum_{L} z c_A V_1 + \sum_{L} z c_B V_2} \]  

(A2-8)

The volume term can be expressed as volume fraction of the reservoir each component occupies. The initial mole fraction of each component in their respective ‘section’ of the reservoir will always be 1. We thus obtain;

\[ x_A \approx \frac{c_A}{c_A + \frac{y_2}{y_1} c_B} \approx \frac{v_B}{v_B + \frac{y_2}{y_1} v_A} \]  

(A2-9)

### A.2.3 Uniform Gradient

In this case, the average distribution of the initial distribution of the initial condition in space is also used in the general equation for the compositional variation.

\[ x_A = \frac{\int_{-L}^{L} c x_A(z) dz}{\int_{-L}^{L} c x_A(z) dz + \int_{-L}^{L} c x_B dz} \]  

(A2-10)

![Figure A.3: Illustration of a Reservoir with an initial uniform concentration gradient with depth.](image)

When the mole fraction of component A varies from 0 at the bottom to 1 at the top of the reservoir with a uniform gradient mole distribution, the mole-fraction of component A can be expressed as;
\[ x_A = \frac{z + L}{2L} \]  \hspace{1cm} (A2-11)

And

\[ c = \frac{1}{v} = \frac{1}{x_A v_A + (1 - x_A) v_B} \]  \hspace{1cm} (A2-12)

Therefore

\[ x_A = \frac{1}{x_A} \begin{pmatrix}
\int_{-L}^{L} z(v_A - v_B) + L(v_A + v_B) \, dz \\
\left[ \int_{-L}^{L} z(v_A - v_B) + L(v_A + v_B) \, dz \right] - \int_{-L}^{L} L - z \\
\left[ \int_{-L}^{L} z(v_A - v_B) + L(v_A + v_B) \, dz \right]
\end{pmatrix} \]  \hspace{1cm} (A2-13)

Integrating this expression yields;

\[ x_A = \frac{A + B}{2B} \]  \hspace{1cm} (A2-14)

Where

\[ A = \left[ \frac{L}{(v_A - v_B)} \ln \left( (v_A - v_B) z + L(v_A + v_B) \right) \right]_{-L}^{L} \]  \hspace{1cm} And

\[ B = \left[ \frac{z}{(v_A - v_B)} - \frac{L(v_A + v_B)}{(v_A - v_B)^2} \ln \left( (v_A - v_B) z + L(v_A + v_B) \right) \right]_{-L}^{L} \]
A.3 The Stefan-Maxwell Equation and its Application

1D Diffusion

For mixtures containing more than two components, \( n \) say, the driving force \( d_i \) for molecular diffusion was derived Taylor and Krishna (1993) in terms of the diffusion flux:

\[
d_i = \sum_{j=1}^{n} \frac{(x_i j_j - x_j j_i)}{c \varphi_{ij}}
\]  

where \( x_i \), \( J_j \), \( c \) and \( \varphi_{ij} \) are the mole fraction of component \( i \), molecular diffusion flux, total concentration of the mixture and the Stefan-Maxwell diffusion coefficient. The reader is reminded that only \( n-1 \) of Eq.1 are independent because \( d_i \) sum to zero, thus only \( n-1 \) of \( J_j \) are independent, thus \( J_n \) can be expressed using:

\[
J_n = -\sum_{i=1}^{n-1} J_i
\]

They showed that is more convenient to express Eq.1 in a dimensional matrix form. The basic set of the 1D diffusion equations in matrix form for \( n \) component system (Amundson et al., 2003):

\[
-c \ddot{\mathbf{d}} = [B] \dot{\mathbf{j}}
\]

where \( \dot{\mathbf{j}} \) is a vector whose elements are the molar flux of each component and \( \ddot{\mathbf{d}} \) is the vector whose components are driving force (compositional gradient) and the elements of \([B]\) are defined by:

\[
B_{ij} = -\frac{x_i}{\varphi_{ij}}, i \neq j
\]
For a ternary mixture this yields:

\[
B_{ii} = \sum_{j=1}^{n} \frac{x_j}{\varphi_{ij}} \tag{A3-5}
\]

Substituting the driving force for the molecular diffusion and Eq. 6 into Eq. 3, we obtain:

\[
[B] = \begin{bmatrix}
-\left(\frac{x_2}{\varphi_{21}} + \frac{x_3}{\varphi_{23}}\right) & \frac{x_1}{\varphi_{12}} & \frac{x_1}{\varphi_{13}} \\
\frac{x_2}{\varphi_{21}} & -\left(\frac{x_1}{\varphi_{21}} + \frac{x_3}{\varphi_{23}}\right) & \frac{x_2}{\varphi_{22}} \\
\frac{x_3}{\varphi_{31}} & \frac{x_3}{\varphi_{23}} & -\left(\frac{x_1}{\varphi_{31}} + \frac{x_2}{\varphi_{32}}\right)
\end{bmatrix} \tag{A3-6}
\]

Substituting the driving force for the molecular diffusion and Eq. 6 into Eq. 3, we obtain:

\[
c[\Gamma]
\begin{bmatrix}
\frac{\partial x_1}{\partial z} \\
\frac{\partial x_2}{\partial z} \\
\frac{\partial x_3}{\partial z}
\end{bmatrix}
= \begin{bmatrix}
-\left(\frac{x_2}{\varphi_{21}} + \frac{x_3}{\varphi_{23}}\right) & \frac{x_1}{\varphi_{12}} & \frac{x_1}{\varphi_{13}} \\
\frac{x_2}{\varphi_{21}} & -\left(\frac{x_1}{\varphi_{21}} + \frac{x_3}{\varphi_{23}}\right) & \frac{x_2}{\varphi_{22}} \\
\frac{x_3}{\varphi_{31}} & \frac{x_3}{\varphi_{23}} & -\left(\frac{x_1}{\varphi_{31}} + \frac{x_2}{\varphi_{32}}\right)
\end{bmatrix}
\begin{bmatrix}
f_1 \\
f_2 \\
f_3
\end{bmatrix} \tag{A3-7}
\]

where \([\Gamma]\) is the thermodynamic factor. In order to calculate the molecular diffusion flux we have to invert \([B]\). We can observe that the matrix is singular since each column will sum to zero, hence the set of differential equations are also singular. The singularity can be circumvented by Eq. 3. Thus any one of the differential equations can be replaced by Eq. 3.

\[
c \begin{bmatrix}
d_1^M \\
d_2^M \\
0
\end{bmatrix}
= \begin{bmatrix}
-\left(\frac{x_2}{\varphi_{21}} + \frac{x_3}{\varphi_{23}}\right) & \frac{x_1}{\varphi_{12}} & \frac{x_1}{\varphi_{13}} \\
\frac{x_2}{\varphi_{21}} & -\left(\frac{x_1}{\varphi_{21}} + \frac{x_3}{\varphi_{23}}\right) & \frac{x_2}{\varphi_{22}} \\
1 & \frac{x_3}{\varphi_{23}} & 1
\end{bmatrix}
\begin{bmatrix}
f_1 \\
f_2 \\
f_3
\end{bmatrix} \tag{A3-8}
\]

where \(d^M\) is given by

\[d^M = \begin{bmatrix}
\Gamma_{11} & \Gamma_{12} & 0 \\
\Gamma_{21} & \Gamma_{22} & 0 \\
0 & 0 & 0
\end{bmatrix} \begin{bmatrix}
d_1^M \\
d_2^M \\
0
\end{bmatrix} \tag{A3-9}\]
Thus:

\[
c \, d_1^M = - \left( \frac{x_2}{\rho_{12}} + \frac{x_3}{\rho_{13}} \right) J_1 + \frac{x_1}{\rho_{12}} J_2 + \frac{x_1}{\rho_{13}} J_3,
\]

\[
c \, d_2^M = \frac{x_2}{\rho_{21}} J_1 + - \left( \frac{x_1}{\rho_{21}} + \frac{x_3}{\rho_{23}} \right) J_2 + \frac{x_2}{\rho_{23}} J_3,
\]

\[0 = J_1 + J_2 + J_3.\] 

This can be extended to pressure and thermal diffusion.

\[
c \begin{pmatrix} d_1^M + d_1^p + d_1^T \\ d_2^M + d_2^p + d_2^T \end{pmatrix} = \begin{pmatrix} - \left( \frac{x_2}{\rho_{12}} + \frac{x_3}{\rho_{13}} \right) & \frac{x_1}{\rho_{12}} & \frac{x_1}{\rho_{13}} \\ \frac{x_2}{\rho_{21}} & - \left( \frac{x_1}{\rho_{21}} + \frac{x_3}{\rho_{23}} \right) & \frac{x_2}{\rho_{23}} \end{pmatrix} \begin{pmatrix} J_1 \\ J_2 \\ J_3 \end{pmatrix}
\]

The vectors for pressure and thermal diffusion flux are:

\[
(d^p) = \begin{pmatrix} x_1(\rho v_1 - M_1)g \\ x_2(\rho v_2 - M_2)g \\ 0 \end{pmatrix}
\]

\[
(d^T) = \begin{pmatrix} \Gamma_{11} & \Gamma_{12} & 0 \\ \Gamma_{21} & \Gamma_{22} & 0 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} k_{T1} \\ k_{T2} \\ 0 \end{pmatrix} \frac{d \ln T}{dz}
\]
A.4 Computing the Diffusivity

The most commonly used forms of expressing molecular diffusion coefficient are based on the Stefan-Maxwell relationship (SM) and Ficks law. In this work, we utilized the Maxwell-Stefan method as this method is easier to implement and this coefficient is also utilized by pressure and thermal diffusion.

For a non-ideal $n$-component mixture, the mole-based SM diffusive flux is given by

$$\left(\mathbf{J}^M\right) = -c[B^M]^{-1} \cdot [\Gamma](\nabla \mathbf{x})$$  \hspace{1cm} \text{(A4-1)}

where $B^M$ is a square matrix. The elements of $B^M$ are given by (Amundson et al., 2003) and is a function of the mole fraction $x_i$ and Stefan-Maxwell diffusion coefficient $\varphi_{ij}$.

$$B^M_{ij} = -\frac{x_i}{\varphi_{ij}}, \quad i = 1, \ldots, n, \ i \neq j$$ \hspace{1cm} \text{(A4-2)}

$$B^M_{ii} = \sum_{k=1}^{n} \frac{x_k}{\varphi_{ik}}, \quad i = 1, \ldots, n$$

$\Gamma$ is the matrix of thermodynamic factors with elements

$$\Gamma_{ij} = x_i \left. \frac{\partial \ln f_i}{\partial x_j} \right|_{x_j, T, P}$$  \hspace{1cm} \text{(A4-3)}

where $f_i$ is the fugacity of component $i$. $\Gamma$ represent the fluid mixture non-ideality (Taylor and Krishna, 1993). This parameter can either be calculated using activity coefficients or an equation of state. Many authors calculate the $\Gamma$ from activity coefficients, which can accurately describe the composition dependency of $\Gamma$, but fail to represent the dependency on pressure (Leahy-Dios and Firoozabadi, 2007). The Peng-Robinson equation of state has a high accuracy for describing the non-ideality for hydrocarbon mixtures.

To calculate the SM diffusion coefficient, we opt to use the correlation proposed by Kooijman and Taylor (1991) for multi-component mixtures based on a generalization of the
Vignes equation for binary systems (Vignes, 1966). For a mixture of n components, this correlation reads:

\[
\varphi_{ij} = \left( D_{ij}^{\infty} \right)^{x_i} \left( D_{ji}^{\infty} \right)^{x_j} \prod_{k=1 \atop k \neq ij}^{n} \left( D_{ik}^{\infty} D_{jk}^{\infty} \right)^{x_{ik} / 2} \quad i, j = 1, \ldots, n
\]

where \( D_{ij}^{\infty} \) are the infinite dilution diffusion coefficients.

We utilize the correlation developed by Leahy-Dios and Firoozabadi (2007) to calculate the infinite dilution coefficients. In their work, they provide a unified model for the calculation of diffusion coefficients of gas, liquids and supercritical states of non-polar multi-component mixtures. Their correlation fits very well to experimental data and produces more accurate results compared to previous correlations (Wilke-Chang, Hayduck-Minhas and Sigmud; to name a few) for all type of mixtures. The expression found by Leahy-Dios and Firoozabadi (2007) is given below:

\[
\frac{cD_{21}^{\infty}}{(cD)^0} = A_0 \left( \frac{T_{r,1} P_{r,2}}{T_{r,2} P_{r,1}} \right)^{A_1} \left( \frac{\mu}{\mu_0} \right)^{A_2 + A_3}
\]

The constants \( A_0 \) to \( A_3 \) are given by

\[
A_0 = e^{-0.0472}
\]

\[
A_1 = 0.103
\]

\[
A_2 = -0.0147 (1 + 10 \omega_1 - \omega_2 + 10 \omega_1 \omega_2)
\]

\[
A_3 = -0.0053 \left( P_{r,1}^{-1.011} - 6 P_{r,2}^{-0.3370} + 6 T_{r,1}^{-1.852} \right) - 0.1914 T_{r,2}^{-0.1852}
\]

\[
+ 0.0103 \left( \frac{T_{r,1} P_{r,2}}{T_{r,2} P_{r,1}} \right)
\]

In Eq. 5, \( c \) is the molar density of component 1, \( \mu \) is the viscosity of component 1, \((cD)^0\) is the product of the dilute gas density and diffusion coefficient, \( \mu_0 \) is the dilute gas viscosity, \( T_{r,i} \) and \( P_{r,i} \) are the reduced temperature and pressure respectively, and \( \omega_i \) are the acentric factor of component i. We calculate \((cD)^0\) using the correlation by Fuller et al. (1966) and the \( \mu_0 \) using the correlation by Stiel and Thodos (1961).
We thus calculate the Fickian diffusion coefficient for an n-component mixture using the following steps:

1. For each binary pair i-j, calculate \( D_{ij}^0 \) from Eq.5;
2. Find \( \varphi_{ij} \) from Eq.4;
3. Calculate \([B^M]\) using Eq.2;
4. Calculate the Fickian coefficient \([D^M]\) by multiplying the inverse of \([B^M]\) by the thermodynamic factor (Eq.3).

Once the Fickian diffusion coefficient is calculated, we can now obtain the molecular, pressure and thermal diffusion flux.

**A.4.1 Computing the Thermodynamic Factor**

The general cubic equation of state:

\[
P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)}
\]

can be rewritten as

\[
Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0
\]

where

\[
A = \frac{aP}{R^2T^2}
\]

\[
B = \frac{bP}{RT}
\]

\[
Z = \frac{Pv}{RT}
\]

Equation 8 gives one or three roots depending on the number of phases in the system. In the two phase region, the largest root is the compressibility factor of the vapour phase while the smallest positive root is that of the liquid.
Eq. 7 at the critical point gives:

\[ a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \]  \hspace{2cm} (A4-12)
\[ b(T_c) = 0.07780 \frac{R T_c}{P_c} \]  \hspace{2cm} (A4-13)
\[ Z_c = 0.307 \]  \hspace{2cm} (A4-14)

At temperatures other than critical:

\[ a(T) = a(T_c), \alpha(T, \omega) \]  \hspace{2cm} (A4-15)
\[ b(T) = b(T_c) \]  \hspace{2cm} (A4-16)

where \( \alpha \) is a function of the reduced temperature and acentric factor.

The fugacity coefficient for a pure mixture is derived by:

\[ \ln \frac{f}{P} = Z - 1 - \ln(Z - B) - \frac{A}{2\sqrt{2}B} \ln \left( \frac{Z + (\sqrt{2} + 1)B}{Z - (\sqrt{2} - 1)B} \right) \]  \hspace{2cm} (A4-17)

For that of a mixture:

\[ \ln \frac{f_i}{x_i P} = \frac{b_i}{b} (Z - 1) - \ln(Z - B) \]
\[ - \frac{A}{2\sqrt{2}B} \left( \frac{2 \sum_j x_j a_{ji}}{a} - \frac{b_i}{b} \right) \ln \left( \frac{Z + (\sqrt{2} + 1)B}{Z - (\sqrt{2} - 1)B} \right) \]  \hspace{2cm} (A4-18)

where the mixing parameters in G-8 and G-18 are defined by the mixing rule:

\[ a = \sum_i \sum_j x_i x_j a_{ij} \]  \hspace{2cm} (A4-19)
\[ b = \sum_i x_i b_i \]  \hspace{2cm} (A4-20)
\[ a_{ij} = (1 - \delta_{ij}) a_i^{1/2} a_j^{1/2} \]  \hspace{2cm} (A4-21)

where \( \delta_{ij} \) is an empirically determined binary interactive parameters. We use Daridon et al., (1992) and Nishiumi et al., (1988) to calculate the BIP for alkane-alkane and alkane-CO\(_2\) systems, respectively.

The solution for the cubic equation of state is described in Ali Danesh (1998) and we can calculate thus calculate the activity coefficient \( \gamma_i \):
The thermodynamic factor is calculated by:

\[ \gamma_i = \frac{f_i}{x_i f} \]

\[ \Gamma_{ij} = \sigma_{ij} + x_i \frac{\partial \ln \gamma_i}{\partial x_j} \bigg|_{T,P,\Sigma} \]
A.5 Dimensionless variables for LJ Potentials

To describe the interactions between fluid particles (spheres) the classical truncated Lennard-Jones 12-6 potential is used in molecular dynamics simulations:

$$U_{LJ} = 4 \varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^{6} \right]$$

where $\sigma$ is the distance at which the potential equals to zero (atomic diameter), $\varepsilon$ is the potential depth and $r$ is the intermolecular distance.

When using Lennard-Jones potentials in simulations, the dimensionless quantities (denoted with a star as superscript) adopts $\sigma$, $M$ and $\varepsilon$ as the units of length, mass and energy, respectively. The table below list the commonly used dimensionless parameters implemented in MD simulations and their computations (Note: $k_B$ is the Boltzmann constant).

<table>
<thead>
<tr>
<th>Property</th>
<th>Dimensionless Form</th>
</tr>
</thead>
<tbody>
<tr>
<td>Length</td>
<td>$r^* = \frac{r}{\sigma}$</td>
</tr>
<tr>
<td>Time</td>
<td>$t^* = \frac{t}{\tau} = t(\frac{\varepsilon}{M\sigma^2})^{1/2}$</td>
</tr>
<tr>
<td>Temperature</td>
<td>$T^* = \frac{k_B T}{\varepsilon}$</td>
</tr>
<tr>
<td>Force</td>
<td>$f^* = \frac{f\sigma}{\varepsilon}$</td>
</tr>
<tr>
<td>Energy</td>
<td>$E^* = \frac{E}{\varepsilon}$</td>
</tr>
<tr>
<td>Pressure</td>
<td>$P^* = \frac{P\sigma^3}{\varepsilon}$</td>
</tr>
<tr>
<td>Number Density</td>
<td>$N^* = N\sigma^3$</td>
</tr>
<tr>
<td>Density</td>
<td>$\rho^* = \frac{\rho\sigma^3}{M}$</td>
</tr>
<tr>
<td>Surface Tension</td>
<td>$\gamma^* = \frac{\gamma\sigma^2}{\varepsilon}$</td>
</tr>
</tbody>
</table>
A.6 Impact of Constant Diffusion Coefficient

From the formulation of the diffusion coefficient it is obvious this parameter is dependent on composition, temperature and pressure. In this section, we shall investigate the effect of assuming the diffusion coefficient is independent on composition has on the timescales of diffusional mixing. It is well established that the diffusion coefficient only affects the timescales and plays no part on the steady state composition profile.

For this exercise we shall use a binary mixture of methane and carbon dioxide. Table G-1 list the properties of the fluid used in our simulations.

<table>
<thead>
<tr>
<th>Fluid Mixture Properties at 410 K and 44.8 Mpa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
</tr>
<tr>
<td>Molar mass (kg.mol⁻¹)</td>
</tr>
<tr>
<td>Molar volume (m³.mol⁻¹)</td>
</tr>
<tr>
<td>Viscosity (mPa.s)</td>
</tr>
</tbody>
</table>

We simulate the binary mixture at isobaric and isothermal conditions under the influence of pressure and molecular diffusion. We initialize the one dimensional domain so that the average composition of methane is 0.14; this is achieved by methane occupying the top 18% of the domain. We run two cases and compare timescales:

1. Variable diffusion coefficient: the molecular diffusion coefficient is dependent on composition.
2. Constant diffusion coefficient: the molecular diffusion coefficient is calculated for a 0.14: 0.86 mixture of methane and CO₂. This diffusion coefficient is then used to calculate the mixing timescales ($4.486 \times 10^{8}$m²/s).
For the system, the infinite dilute coefficient of are: $D_{C_1/CO_2}^\infty = 4.158 \times 10^{-8} \text{ m}^2/\text{s}$ and $D_{CO_2/C_1}^\infty = 7.155 \times 10^{-8} \text{ m}^2/\text{s}$. This gives us a range of values that the diffusion coefficient can occupy for a pure mixture of the two components.

Figure A.4 shows the change in methane composition of 6th the grid point ($z = -1176 \text{ m}$). We observe that both cases reach the same CH$_4$ steady state composition at around the same timescales (variable diffusion = 1058 Myrs and constant diffusion = 1050 Myrs). From this exercise we conclude that diffusion coefficient can be treated as being composition independent.

![Figure A.4: Comparison of the change in methane composition with time for the 6th grid. (o) represent simulation carried out assuming the diffusion coefficient is dependent on composition while the dotted lines represent the simulation carried out using constant composition](image.png)

We also carried out a study on the impact of calculating the molecular diffusion coefficient at isobaric and isothermal conditions. For this exercise, we simulate two cases:

1. Variable diffusion coefficient: the molecular diffusion coefficient is dependent on temperature gradient and pressure gradient. In this case a normal geothermal gradient of -0.03 K/m is imposed and vertical equilibrium is assumed ($P = \rho gh$).
2. Constant diffusion coefficient: molecular diffusion coefficient is calculated under isobaric and isothermal conditions (only dependent on composition) at 410 K and 44.8 × 10^6 Pa.

Figure A.5 shows the change of methane composition of the 6th grid point (z = -1176 m). We observe that both cases reach the same CH₄ steady state composition at around the same timescales (only dependent on composition, isobaric and isothermal = 1190 Myrs and dependent on composition, temperature and pressure gradients = 1198 Myrs). From this exercise we conclude that diffusion coefficient can be calculated assuming the reservoir is isothermal and isobaric.

![Figure A.5: Comparison of the change in methane composition with time for the 6th grid. (o) represent simulation carried out at isobaric and isothermal conditions while the dotted lines represent the case with pressure and temperature gradients.](image-url)
Figure A.6: The stratigraphic correlation chart of the paleozoic section in the western Green River Basin (Stiwell, 1989).
A.8 Geothermal Gradient of the LaBarge

Figure A.7: The geothermal gradient map of the South-western Wyoming Province, south-western Wyoming, north-western Colorado and north-eastern Utah.

The figure above shows the geothermal gradient map of the South-western Wyoming Province, south-western Wyoming, north-western Colorado and north-eastern Utah. The geothermal gradient at the LaBarge Platform (indicated by the cross) is about 1.8°F/100ft which corresponds to 0.0356 K/m (approximately the normal geothermal gradient observed in hydrocarbon reservoirs).
A.9 Thermodynamic Factor for the Quaternary Mixture

Recall that for an \( n \)-component system, the thermodynamic factor is presented by an \( n-1 \) by \( n-1 \) matrix. If we analyze the thermodynamic factor matrix for the average compositions for the quaternary system of CH\(_4\), CO\(_2\), H\(_2\)S and N\(_2\), we notice that this system is ideal-like. The main diagonal terms are order of magnitude bigger than the off-diagonal term is approximately 1. Recall for an ideal mixture the thermodynamic factor is an identity matrix.

\[
\begin{array}{ccc}
0.99921 & 0.07448 & 0.065891 \\
0.00316 & 0.923004 & -0.0737 \\
-0.017896 & -0.012898 & 0.966546 \\
\end{array}
\]

This thermodynamic factor is ideal like.
A.10 Grid Refinement for 3D Analysis

We conducted a grid refinement exercise to select the appropriate grid size for the CMG STARS 3D analysis. We did to mitigate for unnecessary computational effort on the simulator. We initially used a grid size of $80 \times 100 \times 10$ to simulate the fluid mixing in the Madison formation and then used a more refine grid of $120 \times 100 \times 50$ to test whether the former defined grid is sufficient for the simulation. The two grids have approximately 68% NULL blocks. For this exercise we ran the simulation for only 5 million years. The figure below shows the methane separation metric for the two grid setup. We observe that the two curves overlap, thus the less refined grid of $80 \times 100 \times 10$ is sufficient for carrying out the 3D fluid mixing analysis.

![Figure A.8: Grid refinement exercise for the 3D Madison fluid mixing.](image)